VII. *The Electrical Conductivity and other Properties of Sodium Hydroxide in Aqueous Solution as Elucidating the Mechanism of Conduction.*

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Introduction.

In very dilute solutions the relationship between solvent and solute is such as to admit of simple and exact mathematical treatment, and it is in this field that the theory of electrolytic dissociation has been applied with the greatest success. Until recently it was generally believed that the formulæ deduced from a consideration of the properties of very dilute solutions could be applied without any serious loss of accuracy to solutions of moderate concentration. This hope has, however, not been realised. A careful comparative study, especially by Whetham and by Griffiths, of the electrical and osmotic properties of dilute solutions has shown that even at concentrations as low as 0·01 gram-molecule per litre there is a discrepancy between

the values for the coefficient of ionisation deduced by the two methods. It appears, in fact, that the formulæ in which ARRHENIUS's hypothesis has usually found expression, can only be regarded as accurate when applied to solutions containing more than 100 litres of water for each gram-molecule of dissolved salt.

As a qualitative expression, however, the theory is applicable to electrolytes of all kinds, and the development of exact numerical relationships is only hindered by the difficulty of procuring the necessary experimental data, a difficulty that in many cases can only be overcome by the discovery of new methods of investigation. The essential postulate of ARRHENIUS' theory is that a salt may exist both in an active and in an inactive form as regards conductive power, so that when brought into an electrical circuit, only part of the total weight of electrolyte is as a rule directly operative in carrying the current. This conception finds expression in the co-efficient of ionisation, α, which represents the proportion of the salt which is thus active in electrolytic conduction. Independently of any particular theory as to the exact nature of the difference between the ionised and un-ionised part of the salt, the formula $\kappa = m\alpha(u+v)$ is universally applicable as expressing the fact that the specific conductivity κ of any binary compound is dependent on the mass m of the compound contained in unit volume, the proportion α that is able to take part in the transport of the current, and the velocities u and v with which the oppositely charged ions move through the solution under the action of the electrical forces. In the case of dilute aqueous solutions the numerical values of α, u, and v are accurately known. In the case of less dilute solutions they are approximately known. In the case of concentrated solutions and in the case of fused salts they are altogether unknown.

The present paper is essentially a contribution to the study of concentrated aqueous solutions. We hope at some future date to extend the investigation to dilute solutions, but the experiments now described deal almost exclusively with solutions of normal concentration and above. The electrolyte chosen for investigation was sodium hydroxide, which has the advantage, not possessed by many binary salts, of being exceedingly soluble in water, so that even at 0° C. it is possible to measure the properties of a 50-per cent. solution, though at this temperature such a solution is highly supersaturated. In common with others who have been engaged in the study of concentrated aqueous solutions, we have been impressed with the fact that combination between solvent and solute is an essential part of the process of solution, and that the presence of hydrates must be recognised not only in the crystals which separate when the solutions are cooled, but also in the solutions themselves. We have not, however, been able to reconcile our observations with the view, in itself improbable, that this power of combination is no longer operative in dilute solutions, and indeed have obtained evidence that if the reduction in volume which frequently accompanies dissolution may be regarded as an index of the association of solvent and solute, the degree of association reaches a maximum only at dilutions which are not far removed from those required for complete ionisation. We believe, therefore, that

combination with the solvent is an essential part of the process of ionisation, and are of opinion that in the case of dilute aqueous solutions ionisation is simply a final stage in the process of hydrate formation, whereby the hydrated molecule is resolved into two or more hydrated ions. As evidence in support of this view is to be found not only in the observations now recorded, but also in a wide range of current literature, we have reserved the fuller discussion of this theory for a separate communication.

The chief features of the paper may be described under four headings :

(1.) *The Influence of Temperature on Conductivity.*—In our former paper (' Roy. Soc. Proc.,' 1902, vol. 71, pp. 42–54) we were able to give a general curve expressing the relation between conductivity and temperature over the whole range of tempera-ture within which electrolysis is possible. This general curve was arrived at from a consideration of the experimental data with reference to composite electrolytes of all classes, ranging from glass to solutions in liquid ammonia and sulphur dioxide. These scattered observations we were enabled to piece together by a theoretical considera-tion of the influences which determine the change of conductivity with temperature. In the present paper we have been able to give quantitative expression to these different factors, and have obtained results which afford a complete confirmation of our earlier conclusions.

In the formula $\dfrac{\kappa_t}{\kappa_0} = \dfrac{\rho_t}{\rho_0} 10^{-at}(1+bt)^n$, which we have used to represent the relation between specific conductivity and temperature, allowance has been made for each ot the three factors which influence the conductivity. Changes of *concentration* are allowed for by introducing as a factor the ratio ρ_t/ρ_0, which expresses the change ot density between $0°$ and $t°$. Changes of *ionic mobility* have been allowed for by introducing a factor $(1+bt)^n$ similar to that used by SLOTTE to represent the variations of *fluidity* with temperature. Changes in the coefficient of *ionisation* have been allowed for by introducing a factor 10^{-at} similar to that used by ABEGG to express the decay of *specific inductive capacity* as the temperature rises.

Although these factors may not represent perfectly the variations of ionic mobility and of ionisation with temperature, the formula has been found to give a satisfactory representation of the experimental facts over a wide range of temperature. It accurately expresses the varied types of conductivity-temperature curves recorded in the present paper, and indicates not only the point of inflexion which is observed in moderately dilute solutions of sodium hydroxide between $50°$ C. and $100°$ C., but also the maximum conductivity and the second point of inflexion shown in our general conductivity-temperature curve.

Even more important is the fact that by means of this formula it is possible, for the first time as we believe, to analyse the. conductivity-temperature curves for concentrated as well as for dilute solutions, and to estimate separately the effects produced by the increase of mobility and by the decay of ionisation which accompany a rise of temperature.

(2.) *Influence of Viscosity on Conductivity.*—In the conventional method of deducing the coefficient of ionisation from the molecular conductivity by means of the equation $\alpha = \Lambda/\Lambda_\infty$, it is assumed that the ionic mobility is independent of the concentration. As, however, there is a marked difference (amounting to something like 1 per cent.) between the viscosity of water and that of a decinormal salt solution, it is clear that even at this small concentration some appreciable alteration must be looked for in the ionic mobility, and the method is only strictly accurate at concentrations less than N/100. In order to correct for the variation of ionic mobility produced by changes of viscosity, we have assumed as a first approximation that the alterations of mobility are proportional to the alterations in the fluidity of the solution. We have used the term "*intrinsic conductivity*" and the symbol I to represent the ratio obtained by dividing the molecular conductivity by the fluidity of the solution compared with that of water at the same temperature at unity, so that whilst $I = \Lambda/f$, we have $I_\infty = \Lambda_\infty$. The coefficient of ionisation is accurately given by the relation $\alpha = \Lambda/(u+v)$; if $(u+v)/f$ were constant it would also be given accurately by the relation $\alpha = I/I_\infty$; and with the help of this relation we believe that it will be possible to extend the method of determining the coefficient of ionisation from the conductivity to considerably greater concentrations than those within which the validity of the relation $\alpha = \Lambda/\Lambda_\infty$ can be recognised.

The possibility that the ionic mobility might be influenced by the dielectric constant of the medium as well as its viscosity has been discussed by SUTHERLAND (' Phil. Mag.,' 1902, (vi.), vol. 3, p. 161), but cannot be entered into here.

(3.) *Autolytic Conductivity of Dissolved Salts.*—All the acids behave as dielectrics when pure, and only become electrolytes when associated with water or some other "ionising solvent." The alkalies, on the other hand, like the majority of salts, are excellent electrolytes when fused, and are believed to conduct the current quite independently of any interaction with other substances. For the purpose of convenience we propose, at Professor ARMSTRONG'S suggestion, to describe these two classes of electrolytes as *heterolytes* and *autolytes*. It was conceivable that the conductivity of dissolved salts was not wholly dependent on the ionising properties of the solvent, but could be attributed in part to the mere presence of the liquified salt, which could then conduct in the same way as when fused. An important result of the present investigation has been to show that, when a correction for viscosity has been applied, concentrated aqueous solutions of sodium hydroxide exhibit an "intrinsic conductivity" which is too great to be accounted for by the direct influence of the solvent, and which actually increases with the concentration of the soda. This increase we attribute to the autolytic conductivity of the dissolved salt. A similar effect is manifest in the isothermal conductivity-concentration curves for 50° C. and 100° C., which appear to indicate that the fused alkali would be an excellent conductor if over-cooled to these temperatures, and that it contributes largely to the conductivity of the more concentrated solutions. There can be little doubt that

similar influences are at work in the majority of concentrated aqueous salt solutions, but the effects are usually masked by the increased viscosity of these solutions, and very few measurements have been made at concentrations at which the autolytic conductivity of the salt becomes of importance.*

(4.) *Physical Constants of Sodium Hydroxide.*—The available data with reference to the physical properties of the alkalies are more scanty and less accurate than in the case of the more important acids and salts. This result is mainly due to the exceptional difficulty of preparing and standardising pure solutions of these substances. After a long series of experiments we succeeded in devising a method by which it is possible to prepare concentrated solutions of sodium hydroxide directly from weighed quantities of metallic sodium. We were thus enabled to determine some of the physical properties of the solutions with a closer approach to accuracy than has hitherto been attained. This was notably the case with the densities at 18° C. Data are also given, though with a somewhat larger error, for every 10° C. from 0° C. to 100° C. The electrical conductivity at 18° C. was also determined with an accuracy of about 1 part in 1000, and, as the result of experiments on the influence of temperature on conductivity, we are also able to tabulate the conductivities at 0° C., 50° C., 100° C.†

Part I.—Preparation of Concentrated Standard Solutions of Sodium Hydroxide from Metallic Sodium.

Until a few years ago the best material available for experimental purposes was caustic soda purified by dissolution in alcohol. More recently the commercial preparation of metallic sodium has led to the introduction of caustic soda, prepared by the cautious addition to one another of drops of water and particles of sodium in a silver dish; this material contains little impurity except carbon dioxide, and this can readily be removed by means of baryta. Solutions prepared from these materials are necessarily of unknown strength, since the sodium hydroxide is never obtained sufficiently free from moisture and other impurities to be directly weighed out.

Standardisation is usually effected by titrating against an acid of known strength, but this process is liable to serious errors, and we were soon compelled to abandon the attempt to standardise our solutions in this way. Ultimately we were led to

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* Sutherland (*loc. cit.*) observed that in the case of zinc sulphate the ratio $\lambda\eta/\lambda_0\eta_0$, corresponding to our I/I_∞, passed through a minimum value, but attributed this result to altogether different causes.

† The measurements of viscosity given in Part VI. are to be regarded only as approximate determinations. The errors were probably of the order of 1 per cent., but the conclusions based upon these measurements would not have been influenced by much larger errors in the viscosity constants of the solutions. It was considered undesirable to describe in detail a type of viscometer that had not been tested with reference to its applicability to exact measurements.

determine with special care the density of a series of solutions prepared from weighed quantities of metallic sodium and to construct tables, by reference to which it was possible to determine the percentage of sodium hydroxide in any solution with an error amounting to little more than 0·01 per cent. The approximate values previously obtained by titration were then found to be incorrect to the extent of 0·2 per cent. to 0·3 per cent.

The quantitative conversion of sodium into sodium hydroxide was first undertaken on a small scale in order to obtain a reliable standard alkali with which to compare our unknown solutions by titration. But it soon became obvious that a closer approach to purity and accurate standardisation would be attained if we could prepare the whole of the material required for the investigation from weighed quantities of metallic sodium. Quantities of sodium amounting to 50 grammes or 100 grammes were therefore fused and poured into a weighed silver mug ; the mug (which we found must be provided with silver baffle-plates to stop the spray) was placed in a shallow dish of water, covered with a glass shade, and exposed to an atmosphere of steam produced by gently warming the dish. The action proceeded quietly, and the rate at which the sodium was acted upon was indicated by the escape of bubbles of hydrogen from the glass shade. This arrangement proved, however, to be unstable, for ultimately the metal, which had become covered with a layer of caustic soda, floated to the top of the solution and caught fire in the steam, in one case after action had proceeded during about 6 hours, and in a second case after about 30 hours.

In order to avoid this result it would have been necessary to prolong the action during many days. We were therefore led to devise forms of apparatus in which the sodium was suspended in such a way that the caustic soda produced was allowed to flow from the metal, thus maintaining a clean surface and uniform conditions throughout the action. In this way we succeeded, for the first time, in converting a bar of sodium directly into caustic soda, though the method involved the risk that the sodium might become sufficiently heated to melt and flow, with disastrous results, into the water or soda beneath. We were also able to carry out the operation quantitatively, though in a somewhat risky manner, by suspending a weighed quantity of metal in a silver cradle at the top of a large platinum test-tube over a quantity of water which was distilled on to the metal, under reduced pressure, by gently warming the tube. This method was completely successful, but was somewhat tedious in the later stages, owing to the great reduction of vapour-pressure caused by the dissolution of caustic soda in the water. This difficulty was overcome by distilling the water into the platinum tube from a flask, of which the neck was drawn out and bent so as to enter the cover of the tube ; in this form the apparatus was used for preparing some two litres of standard 50-per cent solution.

Some of the details of the method may now be described.

(1.) *Purifying and Weighing the Sodium.*—In order to get rid of oxide and other superficial impurities, the sodium was melted under xylene or paraffin oil, and was

obtained in a clean condition by drawing it up into a short-nosed pipette (previously warmed over a flame to prevent the sodium from solidifying in the tube), and then squirting it into a porcelain basin containing melted paraffin wax. By allowing the wax to solidify, the metal could be kept in a very convenient form, without undergoing any further oxidation. The most convenient method of weighing the metal was to draw it up into a weighed pipette, in which the air had been freed from oxygen and moisture by displacing it through a U-tube containing chips of metallic sodium; in this way it was possible to obtain a known weight of untarnished metal, but in a form in which it could not readily be converted into the hydroxide. We were therefore obliged to modify the method by transferring the melted sodium, before weighing it, from the pipette into a bomb-shaped flask with short narrow neck, in which the air had been freed from moisture and oxygen by suspending in it a fragment of sodium during some hours before the flask was used. In taking the sample of sodium from under the melted paraffin wax, purified air was blown through the pipette to prevent the entrance of paraffin, and after the metal had been sucked up, the outside of the pipette was wiped before allowing the metal to flow into the bomb.

The flasks, which had a volume of about 200 cub. centims., were nearly filled with the molten metal, closed with a small paraffined cork, allowed to cool, and weighed, after momentarily loosening the cork in order to avoid a partial vacuum in the flask during weighing. When required for use the metal was again melted, and poured, at a temperature of about 150° C., into the silver cradle used in converting it into hydroxide. When cold, the flask was again weighed, after momentarily loosening the cork; the difference gave the weight of sodium transferred minus the weight of any oxygen absorbed by the metal in the flask during the operation.

In checking the weight of sodium in the cradle, the metal was protected from the air by a thin cover of silver foil, rapidly cooled by dipping the cradle into cold water, and weighed as quickly as possible. The increase in weight of the cradle gave the weight of metallic sodium plus that of any oxygen absorbed by the metal in the transfer. The two weighings of the sodium differed, therefore, by an amount that was dependent on the sum of the oxidations in the flask and in the cradle. Usually the difference amounted to 10 milligrammes or 15 milligrammes, and only on one occasion rose to 30 milligrammes in consequence of steam produced during the cooling of the cradle obtaining access to the metal under one edge of the silver cover. As the quantity of metal weighed was about 150 grammes, and the oxidation product was not more than 15 milligrammes, the *mean* weight of the sodium was probably correct within 1 part in 20,000. The error due to oxidation was certainly less than that caused by uncertainty in the value of the atomic weight of the metal.

It may be of interest to mention that in pouring the sodium from the bomb into the cradle, the metal always flowed through a thin tube of oxide, reaching from the mouth of the flask to the surface of the metal, and that even if the bomb had contained a considerable quantity of oxidised metal, this could not have been poured

into the cradle, but would have remained adhering to the side of the flask. It may also be mentioned that, whilst steam has a very penetrating action on the metal, a thin film of oxide is sufficient to protect it from oxidation by moderately dry air. We relied largely on the use of considerable weights of metal, amounting in each experiment to about 150 grammes, to render inappreciable the effects of superficial oxidation, and the results which we obtained fully justified this course.

(2.) *Conversion of the Sodium into Hydroxide.*—In order to avoid contamination during the conversion of the sodium into hydroxide, the sodium which had been weighed into the silver cradle was transferred to a platinum vessel, and this vessel was also used for many of the subsequent conductivity measurements. The platinum pot was in the form of a large test-tube, as shown in fig. 1, and held about 500 cub.
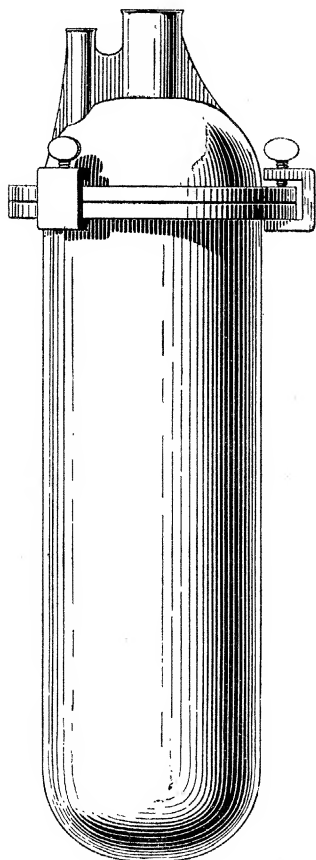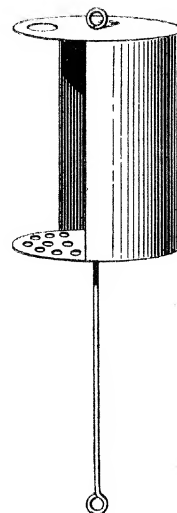
Fig. 1.   Fig. 2.

centims. When used for converting sodium to hydroxide it was provided with a dome-shaped lid, also of platinum, which fitted into the top of the pot. Two cylindrical apertures were provided for admitting the steam and removing the hydrogen. The whole apparatus was thickly coated with silver, electrolytically deposited, in order to resist the pressure of the atmosphere, and the dome-shaped lid was further strengthened by means of silver ribs. An air-tight joint was made

by placing an indiarubber band between the platinum flanges of the lid and the pot ;
these flanges were strengthened by means of heavy silver rings and were held
together by means of three clamps. The silver cradle used to contain the sodium
had the form shown in fig. 2 and occupied the whole of the upper half of the pot.
It consisted essentially of a cylindrical box, $2\frac{1}{4}$ inches in diameter and $3\frac{1}{4}$ inches high ;
one-third of the cylinder was cut away to allow of filling and emptying (this aperture
was covered with silver foil whilst the sodium was weighed) ; the upper surface was
pierced by a circular hole for the admission of steam, and the projecting part of the
lower surface was provided with a series of small holes for the escape of the caustic
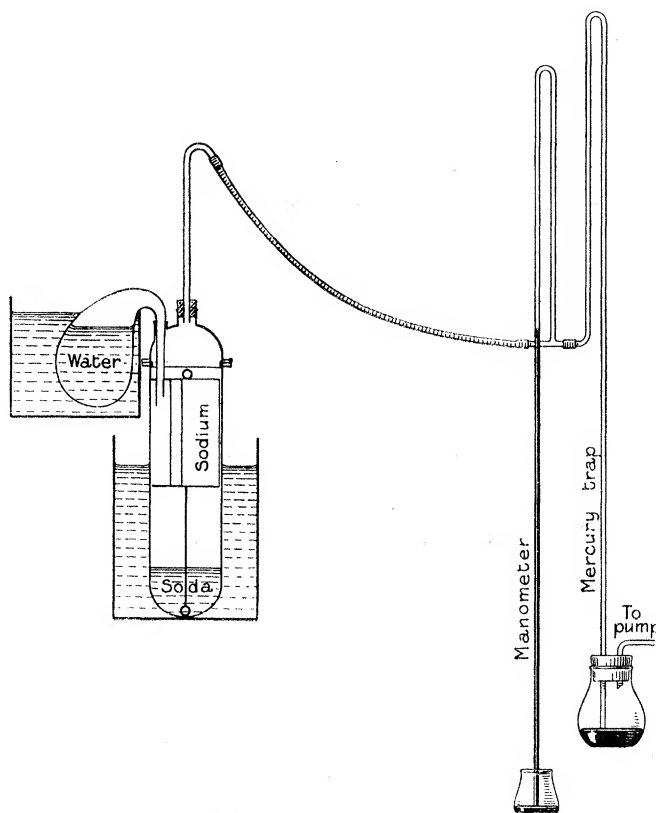
Fig. 3.

soda. A stout silver wire held the cradle in position in the pot, and when the
conversion was complete the cradle was lifted out, inverted and used for mixing the
solution after the soda adhering to the silver wire had been washed down by means
of water.

The arrangement used in effecting the conversion is shown in fig. 3. The pot was
heated to about 45° C. and water was distilled into it under reduced pressure from a
pear-shaped flask heated to about 60° C. in a second water-bath. A manometer was
provided to indicate the pressure, and a mercury trap to prevent water from being
sucked back into the pot if the pump should cease to act. The completion of the
action was marked by the distillation of water, which was condensed in a vertical

tube and allowed to flow back into the pot. As a result of this distillation the upper part of the pot was kept free from soda and no loss was incurred when the flask was removed and the lid of the pot wiped in order to weigh the solution.

The weight of the solution was roughly determined before allowing it to cool, and after adding from a burette the volume of water required to dilute to 50 per cent. a careful weighing was made and the exact percentage calculated. The water required for dilution was also used to rinse the wire of the cradle and the upper parts of the pot. The balance used was sensitive to 0·005 gramme and the weight of the solution was about 400 grammes; the errors of weighing and the slight errors due to variations in the weight of the apparatus were less than those introduced by using the accepted value for the atomic weight of sodium.

In order to illustrate the method, a typical series of weighings may be given :—

Bomb and sodium	= 269·805 grammes.
„ after pouring	= 119·245
Sodium	= 150·560
Cradle and lid and sodium	= 236·978
„ „	= 86·402
Sodium	= 150·576
Total oxidation	= 0·016 gramme.
Mean weight of sodium	= 150·568
Air correction	= 0·166
True weight	= 150·734
Weight of pot, &c., and solution	= 1441·285
„ „ „	= 924·140
Solution	= 517·145
Air correction	= 0·334
True weight of solution	= 517·48 grammes.
Weight of sodium hydroxide	= $150 \cdot 734 \times \dfrac{40 \cdot 06}{23 \cdot 05}$
	= 261·95 grammes.
Concentration of solution	= 50·62 per cent.

(3.) *Purity of the Material.*—Although the method used was calculated to give solutions approaching more nearly to accuracy and purity than those prepared by any other of the available methods, both the sodium and the hydroxide were tested for impurities which might have vitiated the subsequent measurements. By using the metal as raw material it was possible to ensure that the soda contained no acid impurities such as chloride or sulphate, and as the solution was protected from the

air and not allowed to come into contact with glass, it was free, at least initially, from carbonate and silicate. In one experiment the sodium left behind in the cradle a few milligrammes of a black granular metallic residue (possibly iron sawdust introduced in opening the case in which the sodium was packed); although the quantity was probably less than 0·01 per cent. of the weight of sodium, this solution was regarded as of unknown strength and was not used as a standard; in all the remaining experiments the only residue was occasionally a brown stain on the silver cradle. The sodium was therefore free from all but the merest trace of heavy metals.

A further test was made for the presence of alkaline earths. About half a litre of concentrated solution had been allowed to become slightly carbonated, and was decanted from the carbonate that had been precipitated at the bottom of the bottle ; on adding water the precipitate was found to be completely soluble, and there was therefore no appreciable quantity of calcium or magnesium in the metallic sodium or in the hydroxide prepared from it. The presence of a small quantity of potassium or lithium would have had little influence on the subsequent measurements, but a spectroscopic test did not reveal the presence of these elements, and we were therefore led to conclude that the metal we had used as our standard was free not only from acidic impurities, but also from all but traces of foreign metals.

More difficulty was experienced in ascertaining whether the metal might not be alloyed with carbon or hydrogen in the form of carbide or hydride. When decomposed by water, these substances would give rise to volatile products and would not affect the purity of the solutions, but if present in considerable quantities might lead to serious errors in the concentrations. Sodium carbide does not appear to be soluble in metallic sodium, but under certain conditions large quantities of hydrogen may be absorbed. The concordance of our measurements for the density of 50-per cent. solutions of sodium hydroxide prepared from different samples of sodium seemed to indicate that there could not be any large quantity of volatile impurity in the metal, but on the advice of Dr. SCOTT we tried an additional method of purification by heating a sample of sodium in an iron ladle in such a way as to expel any carbide or hydride that might initially be present. The metal was heated until it caught fire and was then poured into melted paraffin wax, but when subsequently converted in the usual way into hydroxide it gave a normal value for the density, and did not appear to have been altered in any way by the roasting. As a matter of fact, metallic sodium is now made almost exclusively by electrolytic processes and no longer contains the black explosive carbide that was formerly associated with it ; even when crude sodium is heated, the black residue that is left in the ladle appears to consist merely of a little lamp-black from the burning petroleum, and if clean metal is used no black scum is produced. A test for acetylene in the gases produced by the action of steam on the metal gave a negative result.

An attempt was made to detect the presence of hydride in the metal by

determining the total loss in weight of the apparatus during the action. In this we were unsuccessful ; the quantity of hydrogen to be weighed was about 6 grammes, and under atmospheric pressure would have occupied some 70 litres ; working under reduced pressure the volume would be increased to about a thousand litres, and our drying apparatus proved to be insufficient to hold back the moisture contained in this large volume of gas. As, however, we considered the possible presence of hydrogen in the metal to be the only serious error to which our method of preparing standard solutions was liable, we were led to devise a further method of testing for this impurity. According to the measurements of TROOST and HAUTEFEUILLE ('Comptes Rendus,' 1874, vol. 78, p. 807), sodium hydride begins to dissociate at a little above 300° C. ; at 330° C. its vapour pressure is 28 millims. and rises to 752 millims. at 420° C. We therefore took a test-tube of hard glass, placed in it 3 grammes of sodium and exhausted by means of a mercury pump. After any occluded gases had been liberated by fusing the metal, the temperature was raised, by means of a bath of fusible alloy, to 550° C, in order to dissociate the hydride, the temperature being recorded by means of a high-pressure mercurial thermometer. In this experiment no gas was liberated. In the second experiment, with 5 grammes of metal, a bubble of gas was obtained which occupied about four-tenths of a cubic centimetre, but was probably air rather than hydrogen. This experiment was conclusive, for the presence of 0·01 per cent. of hydride-hydrogen would have produced 5 cub. centims. of gas, and at the temperature used the whole of this must have been liberated into the vacuum produced by the pump.

We consider, therefore, that whatever impurity may have been present, none was in sufficient quantity to influence our measurements, and that if the atomic weight of sodium be taken as $23·05 \pm 0·005$, the solutions used as standards were accurate within approximately the same limits, that is about 1 part in 5000.

The solutions required for the measurements of density and conductivity at 18° C. were for the most part stored in platinum vessels until required, but, by taking advantage of the relative inertness of the most concentrated solutions, we were enabled to make use of glass bottles for storing the solutions required for determining the temperature coefficients. In consequence, perhaps, of its extreme viscosity and the relatively small amount of water present, a 50-per cent. solution of sodium hydroxide has far less action on glass than a dilute solution. Its density did not alter by a single unit in the fourth place when stored during ten weeks in a glass bottle. A further advantage in the use of concentrated solutions is found in the fact that the carbonate is almost insoluble, and, if produced by exposure to air, separates as a precipitate at the bottom of the bottle, producing a small change in the concentration of the solution, but hardly any depreciation of its purity.

PART II.—DETERMINATION OF THE DENSITY OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE AT 18° C.

Determinations of the density of aqueous solutions of sodium hydroxide have been made by some six different investigators, but owing to the difficulty of preparing pure solutions of known concentration, the results obtained have not been characterised by any close approach to accuracy, and the published tables are far less trustworthy than those for a substance like common salt, which can be weighed out in an anhydrous condition, or sulphuric acid, which can be purified by distillation and freezing. In every case the solutions appear to have been standardised by titration, and it is clear that the errors introduced by inaccurate values for the concentration, and by neutral impurities in the solution, must have been many times greater than those due to the mere measurements of density.

In the early tables of RICHTER (1795) and of DALTON (1810) the density is given to two places of decimals. A more ambitious table was published by TÜNNERMANN in 1827 ('Neues Journal der Pharmacie für Aertzte,' vol. 18, p. 2), in which the percentages of Na_2O were given to three places of decimals (1 part in 30,000) and the densities to four; the additional accuracy of this table is for the most part fictitious, as errors are to be found even in the second place of decimals. TÜNNERMANN's values, in conjunction with those of DALTON, were, however, made use of 30 years later by SCHIFF ('Annalen,' 1858, vol. 107, p. 300), who deduced from them a formula connecting density with concentration, his object being to obtain by extrapolation a value for the density of fused 100-per cent. sodium hydroxide. SCHIFF's formula was used by GERLACH in 1867 ('Zeitschrift für Analytische Chemie,' vol. 8, p. 279) to calculate the densities for each exact percentage of Na_2O and $NaOH$, and GERLACH's table was reproduced in all the dictionaries and text-books of chemistry until 20 years ago.

It is remarkable that the crude measurements of density made in the early years of last century should be still in use; it is even more remarkable that during more than half a century no attempt at revision was made, each successive writer being content to quote from his immediate predecessor the untested figures of a former generation. A revision of the tables of density of sodium hydroxide was attempted by HAGEN, who published in 1883 ('Commentar zur Pharmacopœa Germanica,' Berlin, 1883) a list of densities determined to four places of decimals at no less than 100 concentrations between 0·61 per cent. and 49·02 per cent. NaOH. This list is given in LUNGE's 'Sulphuric Acid and Alkali,' and is quoted thence in the current edition of WATT's Dictionary, but is rather less accurate than the table of GERLACH, which it was intended to replace. It appears, therefore, that until 10 years ago no table had been published in which the density of aqueous solutions of sodium hydroxide was given with a sufficient approach to accuracy to render even the second place of

decimals altogether reliable. All the tables referred to above are quoted in full in COMEY's 'Dictionary of Solubilities.'

The measurements of PICKERING ('Phil. Mag.,' vol. 37, 359, 1894) must be placed in a different category from those described above. As in previous cases, the stock solution was standardised by titration, but it had been prepared from metallic sodium and in all probability was substantially pure. Unusual care appears also to have been taken with the density measurements, which were made at no less than 144 different concentrations between 0 per cent. and 50 per cent. NaOH. No details are given with regard to the titrations, nor is it stated what acid or alkali was used as standard; the author considers, however, that the value for the strength of the stock solution was correct within 0·05 per cent. of the total alkali present. Had this been the case, the density of the 50-per cent. solution should have been correct within 0·0003; actually, however, the value is 0·0013 higher than that which we have found for solutions prepared quantitatively from metallic sodium. The difference in density corresponds to an error of 0·25 per cent. in the determination of the total alkali in the solution, and our own experience has shown us that errors of this magnitude may easily be introduced in standardising an alkali by titration against a standard acid. Although, therefore, PICKERING's relative values for the density at different concentrations must be regarded as substantially accurate, the absolute values (which are given to six places of decimals, and are quoted in this form in WATTS's 'Dictionary of Chemistry') appear to be unreliable to the extent of 0·001 at 50 per cent. NaOH, and roughly to a proportionate extent at the lower concentrations. It is to be regretted that PICKERING did not apply in this case the method, which proved so successful in his determinations of the density of sulphuric acid ('Trans. Chem. Soc.,' 1890, vol. 57, p. 64), of freezing out a hydrate of definite composition and using this to prepare the solutions; an application of this method might have given results as accurate as any that can be obtained by weighing out metallic sodium, and a comparison of the two sets of data would have been of great value.

In weighing out either a hydrate of sodium hydroxide or metallic sodium, it is necessary to introduce an analytical factor based upon atomic weight determinations. As the atomic weights are only known to two places of decimals, it would be useless to pretend to any higher approach to accuracy in the concentration of the solutions used in the density determinations. In the case of sodium hydroxide, this factor may be taken as involving a possible error of about 1 in 5000 in the concentration, corresponding to an error of 0·0001 in the density of a 50-per cent. solution. At the higher concentrations therefore, the densities can only be relied upon to four places of decimals, and in view of the unstable character of the material it is doubtful whether the purity of the solutions would justify a closer approximation, even if the accuracy of the atomic weights should appear to permit it. In a 5-per cent. solution an error of 1 part in 5000 in the concentration would produce the

same effect as an error of 0·00001 in the density, and it is therefore permissible to give the density to 5 places of decimals.

Our original intention was to measure the densities by suspending a cylindrical sinker in the platinum pot, and determining the loss in weight due to the buoyancy of the soda solution. As the sinker had a volume of 100 cub. centims., it was only necessary to measure the loss in weight within a centigramme, in order to determine the density to four places of decimals. It was thought that by adding successive quantities of water from an accurate burette, and checking at the end the total weight of water added, it would be possible to make a rapid series of accurate observations, and to measure the density at frequent intervals over a large range of concentration with little more trouble than that involved in two or three density determinations made by the ordinary method. In this we were disappointed, at least as regards the more concentrated solutions, for

(1.) The viscosity of the 50-per cent. solution was so great that a sensitive balance required several minutes to show a displacement, even when the weight in the pan was altered by 1 centigramme or 2 centigrammes at a time ; and

(2.) The heat generated by the addition of water was so great, and the temperature adjustment so slow, that at least an hour was required before an observation could safely be taken ; a surprisingly large amount of stirring was also required before the solution was sufficiently uniform to give a constant reading.

For these reasons the method, though excellently adapted for more dilute solutions in which there is no marked heat evolution, proved so tedious in case of the concentrated solutions that it was abandoned in favour of a pyknometer. Even when using a pyknometer, the densities of the concentrated solutions could not be determined without considerable trouble, for many hours were required before the freshly diluted solutions were free from minute air bubbles, and the temperature adjustment was so slow that a 50-cub. centim. pyknometer could not safely be adjusted in less than an hour.

Altogether seven standard solutions were independently prepared by the method described in Part I. One of these was used only for conductivity measurements. Density observations were made on all the other six. In order to show the extent of the agreement in the values obtained from these different solutions, a list is subjoined of all the density measurements in the immediate neighbourhood of 50 per cent.

TABLE I.

NaOH.	Density at 18° C.	Density reduced to 50 per cent.	Sample of soda used.
per cent.			
49·99	1·5266$_3$	1·5267	I
49·99	1·5265$_4$	1·5266	III
49·99	1·5269	1·5270	IV
50·00$_2$	1·5268	1·5268	V
49·99$_5$	1·5269	1·5270	IV, V*
49·99$_5$	1·5268$_3$	1·5269	IV, V*
50·00$_4$	1·5267$_5$	1·5267	VI
49·99$_5$	1·5268$_9$	1·5269	IV, V*
50·00$_3$	1·5271	1·5271	VII
50·00	1·5268	1·5268	IV, V, VII*
50·00	1·5268	1·5268	IV, V, VII*
	Mean . . .	1·5268	

The extreme variation from the mean density for the 50-per cent. solution is only 0·0003, and the average error 0·0001, some part at least of which must be attributed to small errors in the measurements of density. We consider therefore that the mean value, 1·5268, for the density of a 50-per cent. solution is correct within 0·0001.

The method adopted for measuring the density of the less concentrated solutions consisted in weighing the standard solution in the pot, diluting with a calculated volume of water, and again weighing to determine the exact concentration. After mixing thoroughly by means of a stirrer, or one of the electrodes described in Part V. of the paper, an Ostwald pyknometer of 50 cub. centims. capacity was filled with the solution, and the remainder was again diluted. Although the weighings were calculated to secure an accuracy of over 1 in 10,000 in the dilution, it was considered desirable after 5 or 6 dilutions had been made to start again from one of the standard 50-per cent. solutions, in order to avoid the influence of cumulative errors such, for instance, as contamination by carbon dioxide. A typical series of weighings will illustrate the method used.

$$
\begin{aligned}
\text{Weight of pot} + 50{\cdot}62 \text{ per cent. solution}. \quad . \quad . \quad . \quad &= 1218{\cdot}97 \text{ grammes.}\\
\text{,,} \qquad \text{,,} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad &= 914{\cdot}95\\
\text{Apparent weight of solution} \quad . \quad . \quad . \quad &= 304{\cdot}02\\
\text{Air} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad &= 0{\cdot}21\\
\text{True weight of solution} . \quad . \quad . \quad . \quad . \quad &= 304{\cdot}23\\
\text{Weight of soda} \quad . \quad . \quad . \quad . \quad . \quad . \quad &= 154{\cdot}00
\end{aligned}
$$

Added 35·58 cub. centims. of water.

* The mixed solutions were stored in a glass bottle; the remainder had not been allowed to come into contact with glass.

Weight of pot and solution . . . . = 1254·56 grammes.

,, ,, ... = 914·95

Apparent weight of solution . . . . = 339·61

Air . . . . = 0·24

True weight of solution . . . . = 339·85

Strength of solution . . . . = 45·31 per cent.

From 50 per cent. to 25 per cent. NaOH the density measurements are considered to be accurate within $\pm 0\cdot 0001$. Altogether 38 determinations were made within this range, usually at intervals of 2·5 per cent. These are set out in Table V. In one or two instances individual measurements showed a discrepancy of as much as 0·0002, but no difficulty was experienced in deciding which figure should be adopted, and in every doubtful case fresh dilutions were made direct from the standard 50-per cent. solution. The measurements made at 25 per cent. and 20 per cent. NaOH are tabulated in order to illustrate the degree of accuracy obtained.

TABLE IIA.

NaOH.	Density.	Density at 25 per cent.	Remarks.
per cent. 25·07	1·2758 s	1·2751	From 30 per cent.
$25\cdot01_7$	$1\cdot2751_5$ p	$1\cdot2750_2$	,, 50 ,,
$25\cdot01_6$	$1\cdot2752_3$ p	$1\cdot2750_7$	,, 50 ,,
$25\cdot03_2$	$1\cdot2753_4$ p	$1\cdot2750_2$	,, 50 ,,
$25\cdot03_2$	$1\cdot2753_2$ p	$1\cdot2750_0$	,, 50 ,,
	Mean	$1\cdot2750_4$	

TABLE IIB.

NaOH.	Density.	Density at 20 per cent.	Remarks.
per cent. 20·00	1·2200 s	1·2200	From 25 per cent.
20·00	1·2202 p	1·2202	,, 25 ,,
$20\cdot00_1$	$1\cdot2204_4$ s	$1\cdot2204_3$	,, 25 ,,
$20\cdot00_1$	$1\cdot2204_1$ p	$1\cdot2204_0$	,, 25 ,,
$20\cdot00_3$	$1\cdot2202_6$ p	$1\cdot2202_3$	,, 50 ,,
$20\cdot00_2$	$1\cdot2202_3$ p	$1\cdot2202_1$	,, 50 ,,
$20\cdot00_2$	$1\cdot2202_6$ p	$1\cdot2202_4$	,, 50 ,,
	Mean	$1\cdot2202_3$	

NOTE.—s = sinker; p = pyknometer.

At the lower concentrations the density measurements are less tedious and more exact, and the strength of the solution is known with sufficient accuracy to justify the inclusion of the fifth place of decimals in the table of density. Within the range from 20 per cent. to 0 per cent., 28 measurements of density were made. Usually two determinations were made with each solution, and the densities deduced from the weighings of the two pyknometers did not differ in any case by more than 0·00002. Within the whole range, from 20 per cent. to 0 per cent., the relative values for the densities are probably exact within 0·00002, but the absolute values are subject to a possible error of about $\pm 0·00005$ in the range from 25 per cent. to 20 per cent. NaOH, $\pm 0·00004$ from 20 per cent. to 15 per cent., and $\pm 0·00003$ from 15 per cent. to 10 per cent.

Interpolation Formulæ.—The curve connecting density and concentration is approximately linear in character, curvature being most marked from 5 per cent. to 0 per cent., and less so in the range from 30 per cent. upwards, but apart from this it does not exhibit special peculiarities. The curve is therefore of little use either for indicating the constitution of the solution or for interpolation. For the latter purpose we have made use of three kinds of sensitive curves.

I. A very convenient means of interpolation consists in recording the extent to which the ordinates of the density curve differ from those of the diagonal line $y = x$ shown in Diagram I. (p. 310). This sensitive curve is obtained by plotting $\rho - (1 + 0·01\,P)$ against P, and has the form shown in the diagram. In using it we have set out the percentage as abscissæ on such a scale that 0·1 per cent. was represented by 1 millim., and the ordinates on such a scale that 1 millim. corresponded to a difference of 0·0001 in the density ; when using this scale, it was easy to read off the density to four places of decimals, and the calculation required was reduced to a minimum. Thus, in reading the density from the curve we have for 49·98 per cent. $\rho - (1 + 0·01\,P) = 0·0268$, and $\rho = 0·0268 + 1 + 0·4998 = 1·5266$.

II. The second sensitive curve represents the deviation of the density curve from a straight line by means of the variations in the tangent of the angle between the radius vector and the axis of concentration. It is obtained by plotting $(\rho - 0·99866)/0·01\,P$ against P, and has the form shown in Diagram I. This curve has the advantage that its sensitiveness increases with the dilution, and it has proved especially useful for interpolation at concentrations at which it was desired to record the fifth place of decimals in the density.

III. Over the range from 5 per cent. to 18 per cent. NaOH the density-percentage curve is a straight line. This is shown by the first sensitive curve, but is entirely masked in the second. The accuracy of the observations may therefore be tested by comparing the values calculated from the linear formula $\rho = \rho_5 + 0·01105\,(P - 5)$ with those which were obtained by interpolation from our experimental values by means of the second sensitive curve.

The result is shown in Table III.

TABLE III.

P.	ρ (experimental).	ρ (calculated).	Difference.
5	1·05454	1·05454	±
6	1·06559	1·06559	±
7	1·07664	1·07664	±
8	1·08769	1·08769	±
9	1·09872	1·09874	+ 2
10	1·10977	1·10979	+ 2
11	1·12082	1·12084	+ 2
12	1·13188	1·13189	+ 1
13	1·14294	1·14294	±
14	1·15400	1·15399	− 1
15	1·16505	1·16504	− 1
16	1·17610	1·17609	− 1
17	1·18714	1·18714	±
18·	1·19817	1·19819	+ 2

In no case does the difference exceed 0·00002, though the absolute values for the density are liable at 18 per cent. NaOH to an error of 0·00004 on account of the fact that the concentration is only known to 1 part in 5000.

Comparison with the Results of other Observers.—With the help of the temperature coefficients deduced in Part III. of the paper, it is possible without any loss of accuracy to calculate the values for the density at 15° C. and so to make a comparison of our results with those of other investigators. This has been done in Table VI. of the paper, in which the densities at 18° C. and 15° C. are given for each exact percentage from 0 to 50. On account both of errors of titration and impurities in the solutions the earlier values are in almost every case higher than those given in Table VI., and the errors extend in some cases even into the second place of decimals.* The deviations from our determination at five typical concentrations are as follows:—

TABLE IV.

NaOH.	TÜNNERMANN (1827).	SCHIFF (1858).‡	KOHLRAUSCH (1879).	HAGER (1883).	PICKERING (1894).
per cent.					
50	—	+ 0·0110	—	+ 0·0121	+ 0·0013
40	+ 0·0050†	+ 0·0022	+ 0·0086	+ 0·0075	+ 0·0008
30	− 0·0001	+ 0·0011	+ 0·0065	+ 0·0030	+ 0·0003
20	+ 0·0214	+ 0·0032	+ 0·0044	+ 0·0032	+ 0·0001
10	+ 0·0009	+ 0·0039	+ 0·0021	+ 0·0047	± .

We had expected that, when corrected for the error due to titration, PICKERING'S values would have shown a close agreement with our own, or, in other words, that the differences between the two series of observations would have been proportional

* See footnote *post*, p. 287.

† 39 per cent. value.

‡ Calculated by means of an interpolation formula from the observations of DALTON and TÜNNERMANN.

to the concentration. This, however, is not the case, as is shown by the differences tabulated in the fourth column of Table VI. Up to 20 per cent. the difference does not exceed 0·0001, and is for the most part negative in sign ; above this concentration the difference is positive, and increases more or less proportionately from 0·0001 at 20 per cent. to 0·0013 at 50 per cent. If the two series of observations had differed only on account of the error introduced by titration, the difference at 25 per cent. should have been half as great as at 50 per cent., and should have amounted to 0·00065 ; actually it amounts only to 0·00027, and as the average error of our five observations at this concentration amounted only to 0·00003, and in the case of PICKERING's observations to only 0·00001, it is clear that the differences are not due exclusively to errors either in the density determinations or in the standardisation of the stock solutions, but must be attributed in part to a difference in purity or some similar cause.

TABLE V.—Density Observations at 18° C.

NaOH.	ρ_{18}.	Sample.	NaOH.	ρ_{18}.	Sample.	NaOH.	ρ_{18}.	Sample.
per cent.			per cent.			per cent.		
51·00	1·5357	IV p	40·00	1·4314	VI s	19·998	1·22016	I p
50·90	1·5352	I s	39·96	1·4310	I s	15·007	1·16520	VI p
50·90	1·5351	I p	37·46	1·4061	V p	15·007	1·16504	VI s
50·62	1·5327	III p	34·95	1·3806	V p	15·007	1·16513	VI p
50·00	1·5268	V p	34·84	1·3795	I s	15·000	1·16480	I s
50·00	1·5267	VI p	32·47	1·3550	V p	14·995	1·16500	IV + V + VII p
50·00	1·5271	VII p	31·85	1·3486	VI p	9·998	1·10953	I s
50·00	1·5270	IV + V p	29·98	1·3289	V p	9·996	1·10972	IV + V + VII p
50·00	1·5269	IV + V p	29·97	1·3287	V p	9·996	1·10973	IV + V + VII p
50·00	1·5269	IV + V p	29·89	1·3276	I s	8·003	1·08771	IV + V + VII p
50·00	1·5268	IV + V + VII p	27·50	1·3022	V p	8·003	1·08772	IV + V + VII p
50·00	1·5268	IV + V + VII p	25·069	1·27580	I s	6·005	1·06563	IV + V + VII p
50·00	1·5268	IV + V + VII p	25·032	1·27533	IV + V + VII p	6·005	1·06565	IV + V + VII p
49·99	1·5266	I s	25·017	1·27515	IV + V p	5·000	1·05475	I s
49·99	1·5265	III p	25·016	1·27523	IV + V p	5·000	1·05466	I p
49·99	1·5269	IV p	24·998	1·27509	VI p	5·000	1·05453	IV + V + VII p
47·49	1·5032	V p	24·977	1·27481	V p	3·996	1·04347	IV + V + VII p
44·99	1·4793	I s	20·003	1·22026	IV + V p	3·847	1·04171	IV + V + VII p
44·99	1·4793	V p	20·002	1·22024	IV + V + VII p	1·9995	1·02126	IV + V + VII p
42·49	1·4555	IV + V p	20·001	1·22044	VI s	1·000	1·01003	IV + V + VII p
42·47	1·4551	V p	20·001	1·22041	VI p	1·000	1·01003	IV + V + VII p
40·00	1·4315	VI p	19·998	1·22003	I s	0·399	1·00322	IV + V + VII p

NOTES.—p = pyknometer, s = sinker. The pyknometer values are the more nearly accurate. The most reliable solutions are those prepared (usually by diluting direct from 50 per cent.) from the mixed solution IV + V + VII. In this series the densities of the solutions were determined by means of two pyknometers. The mean of the duplicate determinations is given above in some cases as if it were a single observation. In no case did these duplicate determinations differ by more than 0·00003. In series V there was some uncertainty in the dilution from 45 per cent. to 42·5 per cent., and the concentration of the solution was therefore re-calculated from its density at 40 per cent. and 20 per cent. ; the intermediate observations are of value for interpolation only.

TABLE VI.—Density of Aqueous Solutions of Sodium Hydroxide at 18° C. and 15° C.

NaOH.	ρ_{18}.	Probable error.	ρ_{15}.	PICKERING'S values exceed these by	H Hydration.	V Solution volume at 18° C.
per cent. 0	0·99866		0·99918	±		
1	1·01003	±0·00002	1·01065	−0·00004	220·1	−0·1257
2	1·02127	±0·00002	1·02198	−0·00006	109·0	−0·1069
3	1·03241	±0·00002	1·03322	−0·00011	71·89	−0·0900
4	1·04349	±0·00002	1·04441	−0·00009	53·36	−0·0742
5	1·05454	±0·00002	1·05554	−0·00008	42·25	−0·0599
6	1·06559	±0·00002	1·06666	−0·00006	34·84	−0·0469
7	1·07664	±0·00002	1·07777	−0·00004	29·55	−0·0347
8	1·08769	±0·00002	1·08887	−0·00001	25·57	−0·0232
9	1·09872	±0·00002	1·09997	±	22·48	−0·0119
10	1·10977	±0·00002	1·11107	±	20·01	−0·0012
11	1·12082	±0·00003	1·12217	±	17·99	+0·0091
12	1·13188	±0·00003	1·13327	−0·00002	16·30	+0·0192
13	1·14294	±0·00003	1·14436	±	14·88	+0·0290
14	1·15400	±0·00003	1·15545	±	13·66	+0·0385
15	1·16505	±0·00003	1·16653	+0·00001	12·60	+0·0479
16	1·17610	±0·00004	1·17761	+0·00001	11·67	+0·0571
17	1·18714	±0·00004	1·18868	+0·00001	10·86	+0·0661
18	1·19817	±0·00004	1·19973	+0·00005	10·13	+0·0750
19	1·20920	±0·00004	1·21079	+0·00007	9·478	+0·0837
20	1·22022	±0·00004	1·22183	+0·00010	8·894	+0·0921
21	1·23121	±0·00005	1·23285	+0·00021	8·365	+0·1007
22	1·24220	±0·00005	1·24386	+0·00026	7·882	+0·1090
23	1·25317	±0·00005	1·25485	+0·00028	7·444	+0·1171
24	1·26412	±0·00005	1·26582	+0·00027	7·042	+0·1252
25	1·27506	±0·00005	1·27679	+0·00027	6·670	+0·1331
26	1·2860	±0·0001	1·2877	+0·0003	6·328	+0·1409
27	1·2968	±0·0001	1·2986	+0·0003	6·012	+0·1486
28	1·3076	±0·0001	1·3094	+0·0003	5·717	+0·1563
29	1·3184	±0·0001	1·3202	+0·0003	5·443	+0·1639
30	1·3290₅	±0·0001	1·3309	+0·0003	5·187	+0·1716
31	1·3396₅	±0·0001	1·3415	+0·0003	4·950	+0·1792
32	1·3502	±0·0001	1·3520	+0·0004	4·725	+0·1866
33	1·3605	±0·0001	1·3624	+0·0006	4·514	+0·1943
34	1·3708₅	±0·0001	1·3728	+0·0007	4·316	+0·2017
35	1·3811	±0·0001	1·3830	+0·0008	4·129	+0·2090
36	1·3913	±0·0001	1·3933	+0·0008	3·953	+0·2164
37	1·4014	±0·0001	1·4034	+0·0009	3·787	+0·2236
38	1·4115	±0·0001	1·4135	+0·0009	3·629	+0·2306
39	1·4215	±0·0001	1·4235	+0·0009	3·478	+0·2376
40	1·4314	±0·0001	1·4334	+0·0009	3·335	+0·2444
41	1·4411	±0·0001	1·4432	+0·0010	3·200	+0·2514
42	1·4508	±0·0001	1·4529	+0·0010	3·071	+0·2583
43	1·4604	±0·0001	1·4025	+0·0011	2·947	+0·2650
44	1·4699	±0·0001	1·4720	+0·0012	2·830	+0·2717
45	1·4794	±0·0001	1·4815	+0·0013	2·718	+0·2782
46	1·4890	±0·0001	1·4911	+0·0013	2·610	+0·2845
47	1·4985	±0·0001	1·5007	+0·0012	2·507	+0·2906
48	1·5080	±0·0001	1·5102	+0·0012	2·409	+0·2967
49	1·5174	±0·0001	1·5196	+0·0013	2·314	+0·3027
50	1·5268	±0·0001	1·5290	+0·0013	2·224	+0·3086

PART III.—INFLUENCE OF TEMPERATURE ON THE DENSITY OF AQUEOUS
SOLUTIONS OF SODIUM HYDROXIDE.

In order to be able to correct the conductivity measurements for changes of concentration produced by alterations of temperature, it was necessary to know not only the density of the solutions at 18° C., but also the variation of density over the whole range from 0° C. to 100° C. The only statement that we have been able to find with reference to the density of caustic soda at temperatures other than 15° C. is a note by HAGER to the effect that the correction for temperature amounts to 0·00045 per degree centigrade from 50 per cent. to 40 per cent., 0·0004 from 29 per cent. to 30 per cent., 0·0003 from 29 per cent. to 20 per cent., and 0·0002 from 19 per cent. to 10 per cent. NaOH. The measurements of the variation of density with temperature, originally undertaken on account of their bearing on the measurements of conductivity, proved to be of some interest on their own account, and were therefore carried considerably further than was originally intended.

No special difficulty was encountered in measuring the density at temperatures up to about 60° C., but at higher temperatures the operation became somewhat troublesome, and the measurements made at the boiling-point were found to be subject to much larger errors than those made at lower temperatures. For the mere purpose of correcting the conductivities for the changes of concentration produced by expansion it would have been sufficient to know the density to three places of decimals, but the fourth place was always determined, and, although the values obtained at the boiling-point were occasionally erratic, we believe that the smoothed values are accurate within a few units in the fourth place.
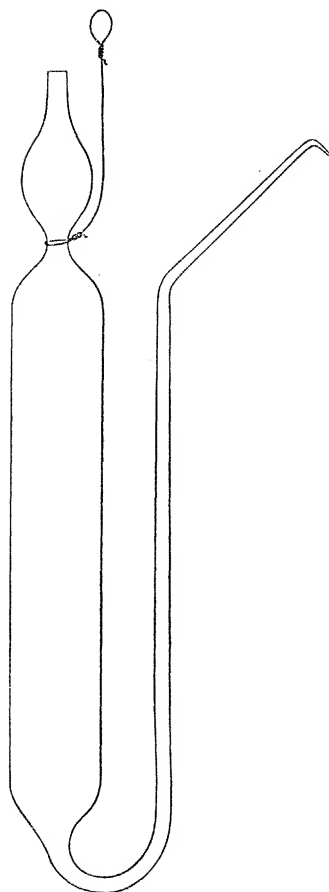
For this series of density measurements we employed a type of density-tube very similar to that described by Dr. PERKIN ('Trans. Chem. Soc.,' 1884, 45, p. 444), the actual form being represented in fig. 4. The bulb is necessary in order to allow for the expansion of the liquid when determining the density at temperatures below that of the atmosphere, but it is also useful at higher temperatures. Only in the case of the most dilute solutions at temperatures in the neighbourhood of the boiling-point was difficulty encountered from the distillation of moisture into the bulb. The tubes used in some of the earlier experiments had a volume of only about 8 cub. centims., but

Fig. 4.

usually the volume was increased to 15 cub. centims. or 25 cub. centims. in order to reduce the errors of adjustment and weighing ; the accuracy of the observations was not very much increased by using larger tubes, and probably the chief source of error arises from fluctuations of temperature. In the case of the concentrated solutions the great viscosity called for the exercise of some degree of patience ; to fill a tube, even with the help of an efficient pump, often required an hour or more, and it was noticed that more than an hour elapsed before a tube of 47 per cent. soda (capacity 25 cub. centims., diameter less than 2 centims.) acquired a steady temperature when cooled in powdered ice. At the lower temperatures the solutions were frequently supersaturated, but we did not experience difficulty on account of crystallisation either in the density tubes or in the conductivity vessels, though occasionally the stock solutions deposited magnificent transparent plates of hydrated soda. From five to ten measurements were made with each solution, the temperature being steadily raised throughout the series ; the error due to the action of the soda on the glass does not appear to be serious, and no change whatever could be detected in the density at 20° C. of a 47-per cent. solution after heating for an hour each at 60° C., at 75° C. and at 100° C.

Form of the Curves. Interpolation Formulæ.—A consideration of the density-temperature curves for a series of percentages beginning with water and ending with 50 per cent. soda showed conclusively that all the relationships could be represented with a close approach to accuracy by equations of the form

$$\rho = \rho_0 + \alpha t + \beta t^2 + \gamma t^3.$$

It was further found that at about 12 per cent. NaOH the coefficient of t^3 vanished, and that thenceforward up to 50 per cent. the relation could be expressed within the limits of experimental error by an equation of the second degree. In order to make these results clear, we append in Table VII. a list of the observed densities for water, decinormal, normal, 26·68 per cent., 34·43 per cent. and 42·54 per cent. NaOH, together with the densities calculated from the cubic or quadratic formulæ. Only in exceptional cases did the observed and calculated densities differ by more than 0·0003, but it is necessary to add that a close agreement on a single series of observations did not necessarily afford a measure of the accuracy of the series, since a serious error at 100° C. might well be masked by an alteration in the coefficients which would not seriously disturb the values calculated for the density at lower temperatures, and would not appear until different series were compared with one another.

For this reason we deemed it very important to check the density-temperature observations by drawing isothermal density-percentage curves for various temperatures and by noting the gradual change in the coefficients of expansion with changing concentration. The temperatures chosen for the isothermal curves were 0° C., 18° C., 50° C., and 100° C., and, having already plotted an accurate isothermal curve for 18° C., it was only necessary now to plot the differences $\rho_0 - \rho_{18}$, $\rho_0 - \rho_{50}$ and $\rho_0 - \rho_{100}$. The

difference curves had the advantage that they could be plotted on a larger scale than the densities, and they were found to be much simpler in form than the sensitive curves described in Part II. of the paper. Where measurements of density had not been made at the exact temperatures chosen for the isothermal curves, values for these temperatures were calculated by means of the cubic or quadratic formulæ described in the preceding paragraph ; the interpolated values, being based to some extent on the whole series of measurements, were at least equal, and probably superior, in value to the individual observations of the series. The difference curves served the double purpose of bringing into relief the experimental errors in measuring the change of density with temperature, and of providing a means of deducing by interpolation the densities for exact percentages at the exact temperatures chosen.

TABLE VII.—Soda Densities, Observed and Calculated.

Water. $\alpha = +0.000043$ $\beta = -0.00000656$ $\gamma = -0.000000020$				Soda Decinormal. $\alpha = -0.00000097$ $\beta = +0.00000594$ $\gamma = -0.000000018$				Soda Normal. $\alpha = -0.0001806$ $\beta = -0.00000394$ $\gamma_2 = -0.0000000108$			
T.	ρ_{18} (observed).	ρ_{18} (calculated).	δ.	T.	ρ_{18} (observed).	ρ_{18} (calculated).	δ.	T.	ρ_{18} (observed).	ρ_{18} (calculated).	δ.
°C.				°C.				°C.			
0	0·9999	0·9999	±	0·0	1·0052	1·0052	±	0·0	1·0468	1·0468	±
4	1·0000	1·0000	±	14·0	1·0041	1·0041	±	15·5	1·0431	1·0431	±
10	0·9997	0·9997	±	25·8	1·0015	1·0013	−2	24·9	1·0401	1·0401	±
20	0·9983	0·9983	±	40·5	0·9967	0·9967	±	40·4	1·0338	1·0338	±
30	0·9958	0·9958	±	50·0	0·9926	0·9927	+1	50·0	1·0295	1·0293	−2
40	0·9924	0·9924	±	76·2	0·9789	0·9787	−2	76·2	1·0154	1·0150	−4
50	0·9882	0·9982	±	99·9	0·9640	0·9640	±	99·7	1·0003	1·0003	±
60	0·9833	0·9832	−1								
70	0·9779	0·9776	−3								
80	0·9719	0·9716	−3		Soda 26·68 per cent. $\alpha = -0.000559$ $\beta = -0.00000067$ $\gamma = 0$				Soda 34·43 per cent. $\alpha = 0.000620$ $\beta = 0.00000043$ $\gamma = 0$		
90	0·9655	0·9652	−3								
100	0·9586	0·9586	±								

Soda 42·55 per cent. $\alpha = -0.000696$ $\beta = 0$ $\gamma = 0$					ρ_{18} (observed).	ρ_{18} (calculated).	δ.	T.	ρ_{18} (observed).	ρ_{18} (calculated).	δ.
T.	ρ_{18} (observed).	ρ_{18} (calculated).	δ.	°C.				°C.			
				0·0	1·3037	1·3037	±	0·0	1·3866	1·3866	±
				12·5	1·2966	1·2966	±	12·8	1·3786	1·3786	±
				15·5	1·2948	1·2949	+1	25·3	1·3707	1·3707	±
°C.				25·0	1·2893	1·2893	±	40·6	1·3607	1·3607	±
0·0	1·4686	1·4686	±	40·6	1·2799	1·2799	±	60·8	1·3472	1·3473	+1
18·0	1·4560	1·4561	+1	50·0	1·2741	1·2741	±	80·0	1·3343	1·3342	−1
29·3	1·4482	1·4482	±	60·0	1·2677	1·2677	±	99·4	1·3207	1·3207	±
49·8	1·4340	1·4439	−1	79·3	1·2552	1·2552	±				
75·0	1·4166	1·4164	−2	98·4	1·2421	1·2422	+1				
100·0	1·3990	1·3990	±								

The observed values for water are taken from WATT's ' Dictionary of Chemistry,' where the values deduced by VOLKMANN from the determinations of HAGEN, MATTHIESEN, PIERRE, KOPP and JOLLY are given to five places of decimals. The differences shown in the table indicate that an additional term must be introduced into the equation $\rho = \rho_0 + \alpha t + \beta t^2 + \gamma t^3$ in order to express the influence of temperature on the density of water correctly to the fourth decimal place.

The values which we have set out for the densities of caustic soda solutions at different temperatures are all based upon the measurements at 18° C. described in Part II. of the paper. The values for 0° C. are deduced from those at 18° C. with the help of the difference curve for $\rho_0 - \rho_{18}$, and as the maximum deviation of any individual experimental values from this curve, as shown in Diagram II., is only 0·0002, we believe that the values for ρ_0 are accurate within 0·0001. This close agreement is of considerable value, as ρ_0 is an important constant in the equation $\rho_t = \rho_0 + \alpha t + \beta t^2 + \gamma t^3$ used in deducing the densities at 10° C., 20° C., 30° C., &c.

The values for 50° C. are deduced from those at 0° C. by means of the difference curve for $\rho_0 - \rho_{50}$; in this case the maximum difference between the experimental values and the curve was 0·0003, and we consider that the values for ρ_{50} are probably accurate within 0·0002.

The values for 100° C. were deduced from those at 0° C. by means of the difference curve for $\rho_0 - \rho_{100}$; in this series the experimental values differ in two cases from those deduced from the curve by as much as 0·001, and the average error amounts to 0·0003, but we consider that the values for 100° C. are probably accurate within 0·0005.

Table VIII. gives the values of $\rho_0 - \rho_{18}$, $\rho_0 - \rho_{50}$, $\rho_0 - \rho_{100}$, which were used for the above purpose; and also the temperature coefficients α, β and γ.

A remarkable confirmation of the substantial accuracy of the values for ρ_{100}, at which temperature the experimental error reaches a maximum, was afforded by the discovery that the values for $\rho_0 - \rho_{100}$ could be represented by the simple logarithmic law

$$\rho_0 - \rho_{100} = \tfrac{1}{25} \log_{10} (P + 11),$$

where P = percentage of soda in solution.

This formula was not in any way used to fix the final values for ρ_{100}, and indeed was not discovered until after these had been tabulated, but the substantial agreement between the two series of values, shown in Table VIII., which do not differ in any case by more than 0·0004, appears to indicate that we have not over-estimated the accuracy of our observations by placing the probable error in ρ_{100} within $\pm$ 0·0005.

TABLE VIII.—Expansion of Aqueous Solutions of Sodium Hydroxide between 0° C. and 100° C.

P.	$\rho_0 - \rho_{18}$	$\rho_0 - \rho_{50}$	$\rho_0 - \rho_{100}$			$\alpha \times 10^6$	$\beta \times 10^8$	$\gamma \times 10^{10}$
			Observed.	Calculated.	Difference.			
0	0·0012	0·0117	0·0413	0·0416	− 3	+ 43	− 656	+ 200
2	31	149	447	446	+1	− 94	− 464	+ 111
4	47	177	473	470	+ 3	− 201	− 339	+ 67
6	57	196	493	492	+1	− 271	− 262	+ 40
8	66	213	511	512	− 1	− 331	− 203	+ 23
10	73	229	528	529	− 1	− 379	− 159	+ 10
12	80	242	544	545	− 1	− 424	− 120	0
14	84	251	558	559	− 1	− 446	− 112	
16	87	260	572	573	− 1	− 467	− 105	
18	91	268	584	585	− 1	− 487	− 97	
20	94	276	596	597	− 1	− 507	− 89	
22	97	283	607	607	±	− 526	− 81	
24	·0100	290	617	618	− 1	− 544	− 73	
26	103	297	627	627	±	− 561	− 66	
28	106	304	636	636	±	− 578	− 58	
30	109	310	645	645	±	− 595	− 50	
32	112	316	654	653	+1	− 612	− 42	
34	114	322	662	661	+1	− 628	− 34	
36	117	328	670	669	+1	− 643	− 27	
38	119	334	678	676	+ 2	− 659	− 19	
40	121	340	685	683	+ 2	− 674	− 11	
42	124	345	692	690	+ 2	− 689	− 3	
44	126	350	698	696	+ 2	− 703	+ 5	
46	128	355	703	703	±	− 715	+ 12	
48	130	359	707	708	− 1	− 727	+ 20	
50	132	362	710	714	− 4	− 738	+ 28	

The coefficients in the equation

$$\rho_t = \rho_0 + \alpha t + \beta t^2 + \gamma t^3,$$

which are also given on Table VIII., were deduced from the final values for ρ_0, ρ_{18}, ρ_{50}, ρ_{100} and were plotted against the percentage of soda in the solution. The resulting curves were quite smooth, with the exception of a break at 12 per cent. which was caused by the change from the cube to the square law ; this break might have been avoided by giving to γ a small negative value above 12 per cent., but as the effect of this on the densities would have been unappreciable, it was thought better not to reintroduce this coefficient when once it had vanished from the equation. These coefficents were used to calculate the density of the solutions for every 2 per cent. at intervals of 10° C. from 0° C. to 100° C., and the results are shown in Table IX. The gradual change in the coefficients is well shown in Diagram II., which also shows the difference curves for $\rho_0 - \rho_{18}$, $\rho_0 - \rho_{50}$ and $\rho_0 - \rho_{100}$.

TABLE IX.—Density of Aqueous Solutions of Sodium Hydroxide between 0° C. and 100° C.

P.	0° C. ±0·0001.	10° C. ±0·0001.	20° C. ±0·0001.	30° C. ±0·0001.	40° C. ±0·0002.	50° C. ±0·0003.	60° C. ±0·0003.	70° C. ±0·0004.	80° C. ±0·0004.	90° C. ±0·0005.	100° C. ±0·0005.
0	0·9999	0·9997	0·9983	0·9958	0·9924	0·9882	0·9833	0·9779	0·9719	0·9655	0·9586
1	1·0124	1·0115	1·0095	1·0069	1·0033	0·9990	0·9941	0·9884	0·9824	0·9760	0·9693
2	1·0244	1·0230	1·0207	1·0177	1·0139	1·0095	1·0045	0·9989	0·9929	0·9865	0·9797
3	1·0364	1·0345	1·0318	1·0285	1·0246	1·0201	1·0150	1·0094	1·0035	0·9970	0·9903
4	1·0482	1·0459	1·0428	1·0393	1·0352	1·0305	1·0254	1·0198	1·0139	1·0075	1·0009
5	1·0598	1·0571	1·0538	1·0501	1·0458	1·0412	1·0359	1·0302	1·0243	1·0179	1·0115
6	1·0713	1·0683	1·0648	1·0609	1·0564	1·0517	1·0463	1·0407	1·0347	1·0284	1·0220
7	1·0828	1·0795	1·0758	1·0717	1·0672	1·0623	1·0569	1·0513	1·0453	1·0390	1·0326
8	1·0943	1·0908	1·0869	1·0826	1·0780	1·0730	1·0676	1·0619	1·0560	1·0497	1·0432
9	1·1057	1·1020	1·0979	1·0934	1·0887	1·0836	1·0782	1·0725	1·0665	1·0602	1·0537
10	1·1171	1·1132	1·1089	1·1043	1·0995	1·0942	1·0889	1·0831	1·0771	1·0708	1·0643
12	1·1399	1·1355	1·1309	1·1261	1·1210	1·1157	1·1101	1·1043	1·0983	1·0920	1·0855
14	1·1624	1·1578	1·1530	1·1480	1·1428	1·1373	1·1316	1·1257	1·1195	1·1132	1·1066
16	1·1849	1·1801	1·1751	1·1699	1·1645	1·1588	1·1531	1·1471	1·1408	1·1343	1·1277
18	1·2073	1·2023	1·1972	1·1918	1·1863	1·1805	1·1746	1·1685	1·1621	1·1556	1·1489
20	1·2296	1·2244	1·2191	1·2136	1·2079	1·2020	1·1960	1·1898	1·1833	1·1768	1·1700
22	1·2519	1·2465	1·2411	1·2354	1·2296	1·2236	1·2174	1·2111	1·2046	1·1980	1·1912
24	1·2741	1·2686	1·2629	1·2571	1·2512	1·2451	1·2388	1·2324	1·2259	1·2192	1·2124
26	1·2963	1·2906	1·2848	1·2789	1·2728	1·2666	1·2603	1·2538	1·2472	1·2405	1·2336
28	1·3182	1·3124	1·3064	1·3002	1·2942	1·2878	1·2814	1·2750	1·2682	1·2615	1·2546
30	1·3400	1·3340	1·3279	1·3217	1·3154	1·3090	1·3025	1·2959	1·2892	1·2824	1·2755
32	1·3614	1·3552	1·3490	1·3427	1·3362	1·3298	1·3232	1·3165	1·3097	1·3029	1·2960
34	1·3823	1·3760	1·3696	1·3632	1·3566	1·3501	1·3434	1·3367	1·3299	1·3230	1·3161
36	1·4030	1·3965	1·3900	1·3835	1·3768	1·3702	1·3634	1·3567	1·3498	1·3429	1·3360
38	1·4234	1·4168	1·4101	1·4035	1·3967	1·3900	1·3832	1·3763	1·3695	1·3626	1·3556
40	1·4435	1·4367	1·4300	1·4232	1·4164	1·4095	1·4027	1·3958	1·3889	1·3820	1·3750
42	1·4632	1·4561	1·4494	1·4425	1·4356	1·4287	1·4217	1·4148	1·4079	1·4009	1·3940
44	1·4825	1·4755	1·4685	1·4615	1·4545	1·4475	1·4405	1·4335	1·4266	1·4196	1·4127
46	1·5018	1·4947	1·4873	1·4805	1·4734	1·4663	1·4593	1·4523	1·4454	1·4384	1·4315
48	1·5210	1·5138	1·5065	1·4994	1·4922	1·4851	1·4781	1·4711	1·4641	1·4572	1·4503
50	1·5400	1·5326	1·5253	1·5181	1·5109	1·5038	1·4967	1·4897	1·4827	1·4759	1·4690

General Results of the Investigation.—Reference may now be made to the more striking results that have followed from the investigation of the influence of temperature on the density of aqueous solutions of caustic soda. The most marked characteristic, which was noticed very early in the investigation, is the great simplification observed in the behaviour of the solutions as the concentration and the temperature are increased. This is indicated by the gradual alteration in the coefficients, but is also shown by the density-temperature curves of Diagram III. The maximum density falls to 0° C. at about 0·6 per cent. NaOH, and is given by the formula as −10° C. at 2 per cent. NaOH. The curves become steadily flatter as the concentration increases, and at 42·8 per cent. the density decreases in a linear manner with the temperature, a behaviour which is in marked contrast to the complex character of the curve that represents the influence of temperature on the density of water. The gradual reduction in curvature, indicated by the decrease with increasing concentration of the coefficient β, was noticed by BREMER ('Rec. Trav. Chim.,' 1887, vol. 7, 268–309) in the case of aqueous solutions of calcium chloride, but our observations show further that β may actually become zero. At still higher concentrations β becomes positive in sign and the curvature is reversed.

Interesting results would doubtless accrue from a comparison of the influence of increased concentration and of increased temperature in straightening out the density-temperature curves. In general terms it may be stated that the curve connecting density and temperature for water between 100° C. and 200° C. would probably be very similar to that for a solution containing 10 per cent. NaOH between 0° C. and 100° C., and that if a solution containing 10 per cent. NaOH were cooled down from 0° C. to −100° C., its behaviour would probably be very similar to that of water between 100° C. and 0° C. The cause of the simplification in behaviour of the concentrated solutions is discussed in connection with the changes of molecular volume described in the following Part IV. of the paper.

PART IV.—THE MOLECULAR VOLUME OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION.

The molecular volumes of dissolved salts are usually much less than those of the solid salts. This contraction cannot be attributed to the mere liquefaction of the salt, as this would probably give rise to an increase of volume, but it may well be attributed to the combination of solvent and solute. In the case of a few compounds, of which the hydroxides of sodium and lithium are by far the most striking examples, the addition of the substance to water actually causes a decrease in the total volume of liquid, and the molecular volume is negative for dilute solutions. In the case of sodium hydroxide the effect of this contraction is remarkable ; it is possible to take a litre of water and dissolve in it no less than 100 grammes of sodium hydroxide without causing any increase in volume, whilst if 50 grammes are added there is actually a contraction of 3 cub. centims.

The solution volumes, V, of 1 gramme of sodium hydroxide at 18° C. are given in the last column of Table VI., together with the *total hydration*, H, of the solution expressed in molecules of water per molecule of soda. When these are plotted against one another, they give the hyperbola-like curve of Diagram IV. The symmetry of this curve, though not exact, is of interest because it appears to indicate that the process of hydration, on which the contraction of volume depends, proceeds continuously from the most concentrated to the most dilute solutions. From this point of view it was of interest to inquire at what dilution the molecular volume would reach its limiting value. A more careful study of the curve of Diagram IV., in conjunction with a similar curve in which the molecular volume was plotted against the logarithm of the hydration, revealed the fact that there was an alteration of curvature at about 45 per cent. NaOH and a further change at about 5 per cent. It was possible, however, to obtain remarkably concordant results for the limiting value of the solution volume by two entirely different methods of extrapolating from the densities between 1 and 5 per cent. The following table shows the agreement between the observed densities and those calculated from the formulæ

$$(a.) \qquad \rho - \rho_0 = 0 \cdot 01141 \mathrm{P} - 0 \cdot 000052 \mathrm{P}^2,$$

$$(b.) \qquad \log_0 \rho/\rho_0 = 0 \cdot 00496 \mathrm{P} - 0 \cdot 000049 \mathrm{P}^2,$$

where ρ_0 is the density of water, ρ the density of the solution, and P the percentage of sodium hydroxide.

TABLE X.

P.	ρ (observed).	ρ (calculated) (a).	Difference.	ρ (calculated) (b).	Difference.
4	1·04349	1·04347	− 2	1·04346	− 3
3	1·03242	1·03242	±	1·03242	±
2	1·02127	1·02127	±	1·02127	±
1	1·01003	1·01002	−1	1·01002	−1
0	0·99866	0·99866	±	0·99866	±

From formula (a) the solution volume is given by the expression

$$\gamma = \frac{1}{\rho_0}\left[1 - \frac{100\,(\alpha - \beta \mathrm{P})}{\rho_0 + \mathrm{P}\,(\alpha - \beta \mathrm{P})}\right], \quad \text{where } \alpha = 0 \cdot 01141,\ \beta = 0 \cdot 000052 \, ;$$

and from formula (b) by the expression

$$\gamma = \frac{1}{\rho_0}\left[1 - \frac{100}{\mathrm{P}}\left(1 - \epsilon^{-\frac{\mathrm{P}}{\mu}(\alpha - \beta \mathrm{P})}\right)\right], \quad \text{where } \mu = 0 \cdot 4343,\ \alpha = 0 \cdot 00496,\ \beta = 0 \cdot 000049.$$

The limiting value deduced from formula (a) is $0 \cdot 1423$, and from formula (b) is $0 \cdot 1427$.

The concordance between these figures renders it probable that they afford an

accurate estimate of the limiting value of the solution volume; the limiting value previously given was 0·145 ('Dictionary of Chemistry,' vol. IV., p. 491). By the same process of extrapolation it can be deduced that the molecular volume does not become constant until a dilution of about 100 litres is reached. The molecular conductivity reaches a maximum value at about 1000 litres, and it is therefore clear that the decrease of molecular volume proceeds side by side with the process of ionisation, and does not cease until the latter is almost complete.

A study of the influence of temperature on the solution volume of sodium hydroxide gave somewhat remarkable results. Instead of increasing steadily from 0° C. to 100° C., as was expected, the solution volume at all percentages was found to reach a maximum value at 60° C. to 70° C., and then to decrease between 70° C. and 100° C.

There is thus a close resemblance between the solution volume at 90° C. and that at 30° C. The extent of the variation produced by alterations of temperature decreases with increasing concentration, and at 50 per cent. NaOH amounts only to 7 per cent. The data for the solution volume are given in Table XI. and are represented graphically in diagrams V. and VI.

In discussing the significance of the variations of solution volume it may be regarded as certain that the great variation in the case of dilute, as compared with concentrated, solutions must be attributed to the complex character of liquid water and not to any complexity introduced by the addition of soda. It appears, in fact, that the maximum of simplicity is reached in a 50-per cent. solution at 100° C., and that the most complex solution with which we have to deal is water.

The complex character of the water molecule was demonstrated by RAOULT ('Ann. Chim. Phys.,' 1884, (6), vol. 2, p. 66), and was made use of by RÖNTGEN ('Wied. Ann.,' 1891, vol. 45, p. 91), who attributed the increase of density between 0° C. and 4° C. to the dissociation of "ice molecules" having a greater molecular volume than the water molecules. This view was elaborated by SUTHERLAND ('Phil. Mag.,' 1900, vol. 50, p. 460), who suggested that RÖNTGEN's ice molecules had the formula H_6O_3 and might be called *trihydrol*, whilst the water molecules consisted of *dihydrol*, H_4O_2. A further discussion is given by STRADLING ('Jour. Frank. Inst.,' 1901, vol. 152, pp. 257–268) with reference especially to the compressibility of water. It is probable that the simplification in the density-temperature curves of the preceding Part III. of the paper, which results from the addition of soda or from an increase of temperature, is due primarily to the destruction of the ice molecules to which water owes most of its abnormal properties. A similar explanation may be given of the large negative solution volume of sodium hydroxide, which is most pronounced at those low temperatures at which the water contains a large proportion of the bulky ice molecules. This explanation does not, however, in any way account for the fact that the molecular volume of sodium hydroxide decreases from 70° C. to 100° C. The only explanation that we can offer to account for this unexpected behaviour is that over this range of temperature the water contains a large proportion of steam

molecules, having the simple formula H_2O, that these, like the ice molecules, have a larger molecular volume than the water molecules, and are destroyed by adding soda to the solution. The addition of soda may then be regarded as simplifying the solution mainly by lessening the proportion of associated and dissociated water molecules, the water molecules themselves being converted into hydrates of soda having somewhat similar properties to *dihydrol*, but an even smaller molecular volume. This view, which is an extension of the theories of RÖNTGEN and of SUTHERLAND, appears to be fully justified by the experimental facts, and indeed it is difficult to avoid the conclusion that in the neighbourhood of the boiling-point the simple steam molecules form, if not the largest, at least a very important proportion of the total number.

TABLE XI.—Solution Volume of 1 gramme of Sodium Hydroxide between 0° C. and 100° C.*

	0° C.	10° C.	20° C.	30° C.	40° C.	50° C.	60° C.	70° C.	80° C.	90° C.	100° C.
2	− ·20	− ·14	− ·10	− ·08	− ·06	− ·05	− ·06	− ·06	− ·07	− ·08	− ·09
3	− ·17	− ·12	− ·08	− ·06	− ·05	− ·04	− ·04	− ·05	− ·06	− ·06	− ·07
4	− ·15	− ·10	− ·07	− ·05	− ·03	− ·03	− ·03	− ·03	− ·04	− ·05	− ·06
5	− ·13	− ·09	− ·05	− ·03	− ·02	− ·02	− ·02	− ·02	− ·03	− ·04	− ·05
6	− ·111	− ·071	− ·041	− ·023	− ·010	− ·006	− ·005	− ·006	− ·012	− ·020	− ·036
7	− ·092	− ·056	− ·029	− ·012	− ·002	+ ·003	+ ·004	− ·003	− ·003	− ·012	− ·025
8	− ·078	− ·044	− ·019	− ·003	+ ·007	+ ·013	+ ·013	+ ·007	+ ·004	− ·003	− ·014
9	− ·064	− ·033	− ·009	+ ·007	+ ·017	+ ·023	+ ·020	+ ·017	+ ·011	+ ·004	− ·003
10	− ·049	− ·020	+ ·003	+ ·018	+ ·026	+ ·032	+ ·030	+ ·027	+ ·021	+ ·014	+ ·007
12	− ·023	+ ·003	+ ·030	+ ·036	+ ·044	+ ·048	+ ·049	+ ·047	+ ·042	+ ·035	+ ·027
14	+ ·001	+ ·025	+ ·042	+ ·053	+ ·060	+ ·064	+ ·065	+ ·064	+ ·060	+ ·054	+ ·047
20	+ ·066	+ ·082	+ ·095	+ ·103	+ ·109	+ ·112	+ ·114	+ ·112	+ ·110	+ ·106	+ ·101
30	+ ·154	+ ·165	+ ·173	+ ·179	+ ·183	+ ·185	+ ·186	+ ·186	+ ·185	+ ·183	+ ·179
40	+ ·236	+ ·243	+ ·250	+ ·254	+ ·257	+ ·260	+ ·261	+ ·261	+ ·260	+ ·260	+ ·257
50	+ ·299	+ ·305	+ ·310	+ ·313	+ ·316	+ ·317	+ ·319	+ ·322	+ ·320	+ ·319	+ ·318

PART V.—THE CONDUCTIVITY OF SODIUM HYDROXIDE IN AQUEOUS SOLUTION AT 18° C.

The only measurements that we have been able to find of the electrical conductivity of sodium hydroxide in aqueous solution, apart from a single measurement by LOOMIS ('Ann. Phys. Chem.,' 1897, vol. 60, p. 550) of the specific conductivity and density of a normal solution, are those of KOHLRAUSCH ('Wied. Ann.,' 1897, vol. 6, pp. 1 and 145 ; 1885, vol. 26, p. 161). As, however, the values given by KOHLRAUSCH for the densities are considerably higher than those which we have deduced in Part II. of this paper, it would seem that the accuracy of the electrical measurements was very largely neutralised by the presence of neutral impurities in the

* Our thanks are due to Mr. R. L. QUERTIER for his help in calculating Tables IX. and XI. [December, 1904.—The first four rows of figures have been amended.]

solution* or by errors introduced in standardising the solutions by titration. We have therefore redetermined the conductivities at 18° C., and although our electrical measurements are probably not so accurate as those of KOHLRAUSCH, we consider that the purity and accuracy of our solutions and the increased number of observations combine to render our measurements at 18° C. more reliable than those previously recorded.

Fig. 5.

(1.) *The Solutions* used for the electrical measurements were similar to those employed in measuring the density, and indeed in one series of dilutions the same solutions were used for measuring the two properties. As it was likely that the conductivity would be influenced more than the density if the alkali should become partially neutralised by carbonic or silicic acid, special care was taken to maintain as far as possible the original purity of the solutions. The solutions used in measuring the conductivity from 50 per cent. to 20 per cent. were kept in platinum vessels and only allowed to come into contact with the glass of the electrode that was introduced in measuring the conductivity. The solutions below 20 per cent. were made up from standard solutions which had been kept in platinum or stored in a glass bottle as 50-per cent. solutions during periods ranging from a few days up to two months, but as the density remained unchanged at the end of ten weeks, and the maximum conductivity measured at the end of five months was within 0·1 per cent. of the value obtained before transferring to the glass bottle, it is believed that no appreciable fouling had resulted from the contact of the viscous 50-per cent. solution with the glass.
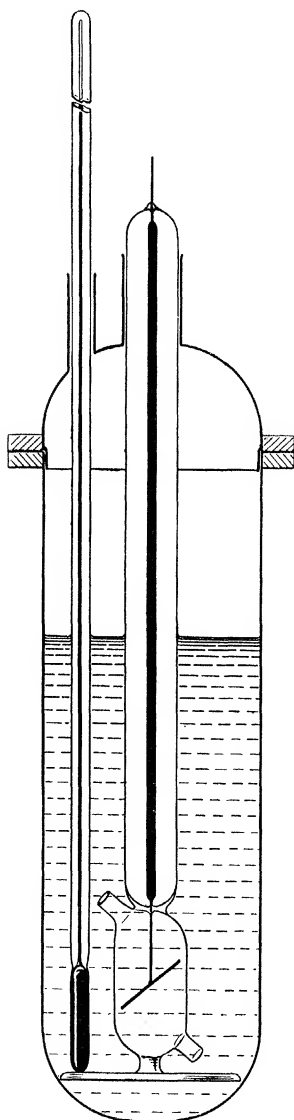
(2.) *The Conductivity Vessel.*—No difficulty is experienced in designing a conductivity apparatus of *low* resistance capacity in which the liquid is allowed to come into contact only with platinum surfaces, but it is very difficult, perhaps even impossible, to design a simple apparatus of this kind in which the resistance capacity is sufficiently large to give satisfactory measurements with solutions of high conductivity. We were able, however, to effect a very satisfactory compromise by making use of the platinum vessel already described and introducing into it an electrode shielded within a glass tube of suitable shape. The total area of glass in the electrode was comparatively small, and 300 cub. centims. to 400 cub. centims. of solution was used for each observation. Under these conditions the fouling of the solution by contact with the glass of the

* See footnote, p. 287.

electrode must have been very slight.   The surface of the platinum pot was used as the second electrode.*

(3.) *Calibration of the Electrode.*—The majority of the measurements at 18° C. were made with an electrode having the form shown in fig. 5.   The required resistance capacity was obtained by suitably fixing the length and cross section of the tubes leading outwards from the electrode.   The electrode most used was one which had a resistance capacity of 13·74.   For calibrating it a normal solution of potassium chloride was used and two series of measurements gave the capacity as

(1.) 13·738 with 200 cub. centims. of solution in the pot, and

(2.) 13·735 with 300 cub. centims. of solution.

A very valuable check on the accuracy of the calibration was obtained by comparing the values for the specific conductivity of the solutions as deduced from measurements with different electrodes.   Using a carefully calibrated electrode of the type described in Part VI. of the paper as a standard, the capacity deduced from measurements of the maximum conductivity of caustic soda was 0·05 per cent. higher,

* *Fouling of the Solutions.*—(1.) The possibility has been suggested that the electrical measurements might have been vitiated by impurities introduced by the contact of the soda with the glass of the electrodes. Such fouling might have occurred if the electrode figured above had been heated with the solution during several hours.   This, however, was not the case, as this electrode was used exclusively for low-temperature measurements, and was removed from the solution when not in use.   At atmospheric temperatures the fouling is exceedingly slow, and the experiments quoted on p. 284 may be regarded as affording experimental justification of the view that no appreciable fouling could have taken place in the short period of time during which the electrode was in contact with the solution.

(2.) The advantages which we believe to have resulted from the use of a platinum vessel with glass-cased electrode over a glass cell of the ordinary kind may be briefly indicated :—

(*a*) It is reasonable to suppose that under comparable conditions the total fouling is proportional to the surface of glass exposed to the solvent action of the soda, but is not directly dependent on the volume of the solution.   If this be so, the percentage error due to fouling would be inversely proportional to the volume of the solution, and by using 300 cub. centims. or 400 cub. centims. in place of 10 cub. centims. or 20 cub. centims. the risk of fouling would be proportionately reduced.   The electrode was used as a stirrer and was frequently drawn above the surface of the solution so as to be completely emptied ; there was therefore no local fouling.

(*b*) Although the fouling at atmospheric temperatures is too slow to be easily detected, the advantages of the platinum vessels were clearly demonstrated in the experiments at higher temperatures, described in Part VII. of the paper.   Solutions heated in glass vessels showed a change of conductivity amounting in some instances to as much as 1·6 per cent. (p. 300), but with platinum vessels this source of error was altogether eliminated (p. 300).   Thus, in an actual experiment with the electrode figured opposite, the initial resistance at 18° C. of the solution was 169·2 ohms; after making eight observations between 18° C. and 100° C. the final resistance was still 169·2 ohms.   This experiment not only shows the superiority of the platinum vessel, but also justifies the conclusion that at low temperatures the fouling of the solution by contact with the glass of the electrode must have been very slight.

The final experiments quoted in Part VII. were made with the electrode figured on p. 298, fig. 9, which had an even smaller surface of glass.

and from measurements of a 45-per cent. solution 0·01 per cent. higher than the value given above.

(4.) *The Measurements of Conductivity.*—The resistances of the solutions were measured by using an alternating current and a telephone. The wheel-bridge recommended by KOHLRAUSCH (KOHLRAUSCH and HOLBORN, ' Leitvermögen der Elektrolyte,' p. 42) was used and found to be both convenient and accurate. The main disadvantage of the bridge is that the sensitiveness decreases considerably when used in comparing unequal resistances, and that the bridge-wire must be carefully calibrated at intervals of a few months if the instrument is in constant use. These difficulties were overcome by using the comparison coils (1, 10, 100, 1000 and 10,000 ohms) supplied with the bridge only in determining the approximate resistance of the electrolyte, whilst the final measurements were made by comparison with an equal resistance. The resistance-box used for this purpose was specially wound so as to be almost free from electrostatic capacity. The exact position of silence on the bridge-wire was determined with three resistances differing slightly from one another, and in this way three readings were obtained, from each of which it was possible to calculate the resistance. As the readings were all close to the centre of the wire, a maximum of sensitiveness was obtained, and it was only necessary to check from time to time the exact position of the electrical centre of the bridge-wire. The three readings were usually concordant within one or two parts in 10,000, and if necessary were repeated until concordant results were obtained. The method may be illustrated by an example taken from a recent series of measurements.

Resistance of coils.	Reading of bridge-wire.	Resistance (ohms).
140·5	500·2	140·61
140·4	500·3	140·57
140·6	500·0	140·60

Mean . . .	140·59
Leads . . .	0·10
	140·49

Resistance capacity 13·738 cm.$^{-1}$; specific conductivity $\kappa_{18} = 0·09775$ cm. ohm^{-1}.

Concordant readings of the instrument do not necessarily indicate a corresponding approach to accuracy in the values deduced for the conductivity of the electrolyte. The errors due to heating, polarisation, self-induction, and capacity are fully discussed by KOHLRAUSCH and HOLBORN in the volume already referred to (pp. 54–59). Of these the most serious are those due to polarisation when the resistance is low, and to electrostatic capacity when the resistance is high. In our experience the most favourable resistance to measure is about 50 ohms to 100 ohms, but in determining the conductivity of a solution over a range of temperature involving large changes in conductivity we have occasionally been obliged to measure resistances as high as

1000 ohms and as low as 5 ohms. The resistance of the leads was reduced as far as possible by employing stout copper rods to connect the bridge with the vessel, and by using copper enclosed in glass, rather than platinum, for the leads inside the conductivity vessel; there was, however, some loss of accuracy when the resistance to be measured was much below 10 ohms. To measure resistances above 500 ohms it was necessary to introduce a correction for the slight electrostatic capacity of the coils of the resistance box; the correction was determined by stretching a thin wire resistance of 2000 ohms or 3000 ohms over the ceiling in such a way as to be free from capacity and then measuring its apparent resistance (1) by a direct current and galvanometer, and (2) by an alternating current and telephone; the difference gave the correction to be applied to the readings of the telephone, and this correction was found to be proportional to the resistance measured.

Taking into account the various sources of error to which the measurement of the electrolytic conductivity of solutions of varying concentrations is liable, we consider the general accuracy of our tabulated results for 18° C. may be taken to be within 1 part in 1000, although an inspection of Diagram VII., in which all the observations are set out, shows that there are some individual readings which are below this standard.

The results obtained in measuring the conductivity of aqueous solutions of sodium hydroxide at 18° C. are shown in Tables XII. and XIII., and are plotted out in Diagram VII., together with the values given by KOHLRAUSCH. The maximum conductivity, $\kappa_{18} = 0\cdot3490$, is at about 15 per cent. NaOH, but there is no substantial alteration of conductivity between 14·9 per cent. and 15·6 per cent. KOHLRAUSCH'S value for 15 per cent. is 0·3463. For a normal solution LOOMIS gives $\rho_{18} = 1\cdot0418$, $\kappa_{18} = 0\cdot145$, whilst our values are $\rho_{18} = 1\cdot04172$, $\kappa_{18} = 0\cdot1575$.

The values given by KOHLRAUSCH are shown on Diagram VII. by open circles, plotted out in reference to the percentages given by him. If the position of these circles be shifted to the percentages deduced from the densities given by KOHLRAUSCH, most of the observations come very nearly on to our own curve, but the uncorrected values differ by as much as 0·0053 on 0·1560 at 35 per cent. NaOH. KOHLRAUSCH'S value for the maximum, which should not be affected by errors of concentration, differs from ours by nearly 1 per cent., and it is therefore probable that his solutions contained appreciable quantities of neutral impurities.*

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* Prior to the introduction of metallic sodium as a source of purified caustic soda this alkali was made by the action of lime upon sodium carbonate. In concentrated solutions the interaction

$$Na_2CO_3 + Ca(OH)_2 = 2NaOH + CaCO_3$$
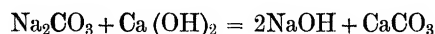
is probably reversible and the solution would therefore contain a definite proportion of sodium carbonate, in addition to traces of calcium salts. In this way it is possible to account for the wide difference that exists between the densities tabulated by SCHIFF, KOHLRAUSCH and HAGEN, and the later observations, tabulated by PICKERING, and those in the present paper, in which the alkali was prepared from metallic sodium.

TABLE XII.—Conductivity Observations at 18° C.

P.	κ_{18}.	Solution.	P.	κ_{18}.	Solution.	P.	κ_{18}.	Solution.
9·998	·3091	I	14·28	·3470	II	15·01	·3491	IV, V
5·000	·1944	I	11·70	·3307	II			
50·90	·07972	I	10·07	·3099	II	50·00	·08203	IV, V, VII
			8·711	·2872	II	25·03	·2713	IV, V, VII
			7·677	·2656	II	20·00	·3284	IV, V, VII
50·62	·08034	II	5·002	·19456	II	15·00	·3490	IV, V, VII
50·62	·08031	II	2·502	·10802	II	9·996	·3092	IV, V, VII
45·31	·09629	II				8·003	·2730	IV, V, VII
40·28	·11834	II				6·005	·2243	IV, V, VII
35·24	·15346	II	50·00	·08203	V	5·000	·1954	IV, V, VII
30·21	·2045	II	47·49	·08958	V	3·996	·1627	IV, V, VII
25·17	·2682	II	44·99	·09775	V	2·000	·08864	IV, V, VII
20·14	·3255	II	42·48	·1078	V	1·000	·04660	IV, V, VII
16·75	·3469	II	40·00	·1206	V	3·000	·12708	IV, V, VII
16·43	·3475	II	37·46	·1364	V	0·9997	·04656	IV, V, VII
16·16	·3483	II	34·95	·1564	V	3·847	·15748	IV, V, VII
15·90	·3485	II	32·47	·1803	V	3·847	·15755	IV, V, VII
15·64	·3491	II	29·97	·2078	V	19·96	·3272	IV, V, VII
15·40	·3490	II	27·50	·2387	V	46·74	·09235	IV, V, VII
15·16	·3489	II	24·98	·2712	V	39·72	·12245	IV, V, VII
14·93	·3489	II				29·76	·2114	IV, V, VII
14·71	·3485	II				14·96	·3493	IV, V, VII
14·49	·3475	II	50·00	·08203	VI	43·56	·10384	IV, V, VII

TABLE XIII.—Specific, Molecular and Intrinsic Conductivities of Sodium Hydroxide at Exact Percentages.

NaOH.	Concentration. m.	Specific conductivity.		Molecular conductivity. Λ.	Fluidity. f.	Intrinsic conductivity. I.
		κ_{18}.	κ_{18} (KOHLRAUSCH).			
Per cent.						
50	19·06	0·08203	—	4·30	0·01417	303·7
47·5	17·83	0·08953	—	5·02	0·01724	291·3
45	16·62	0·09771	—	5·88	0·0212	277·4
42·5	15·44	0·1077	—	6·97	0·0253	275·7
40	14·29	0·1206	0·1164	8·44	0·0310	272·2
37·5	13·167	0·1361	—	10·34	0·0385	269·4
35	12·067	0·1560	0·1507	12·93	0·0485	266·4
32·5	10·996	0·1798	—	16·35	0·0637	256·7
30	9·954	0·2074	0·2022	20·83	0·0866	240·5
27·5	8·939	0·2386	—	26·69	0·0112	238·3
25	7·957	0·2717	0·2717	34·22	0·0145	236·0
20	6·092	0·3284	0·3272	53·95	0·0270	199·6
15	4·363	0·3490	0·3463	80·00	0·0415	192·8
10	2·770	0·3093	0·3124	111·7	0·0610	183·1
8	2·1722	0·2729	—	125·6	0·0688	182·5
6	1·5961	0·2242	—	140·5	0·766	183·4
5	1·3163	0·1954	0·1969	148·4	0·805	184·3
4	1·0420	0·1628	—	156·3	0·844	185·2
2	0·5099	0·08866	—	173·7	0·922	188·4
1	0·2522	0·04653	—	184·5	0·961	192·0
0	—	—	—	218 (?)	1·000	218 (?)

PART VI.—THE VISCOSITY AND INTRINSIC CONDUCTIVITY OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE.

Reference has been made in the earlier parts of the paper to the great viscosity of concentrated solutions of sodium hydroxide, which indeed manifests itself even in so simple an operation as filling and emptying a pipette. As this was likely to have a great effect upon the ionic mobility, a series of measurements of viscosity was made, with the help of which it was hoped that it might be possible to correct the observed conductivities for the influence of viscosity.

Relation between Conductivity, Ionisation and Ionic Mobility.—The usual mode of expressing the relationship between conductivity and ionic velocities is derived from the consideration of the flow of electricity from side to side of a unit cube of the electrolyte under a potential gradient of 1 volt per centim. Thus if U and V are the ionic velocities under such a potential gradient, m the concentration of the solute in gramme equivalents per litre (and therefore $m/1000$ the number of gramme equivalents in the unit cube), α the fraction of the solute that is in the ionised or current-carrying state, and q the quantity of electricity of either sign liberated by 1 gramme equivalent of any monad ($q = 98360$ coulombs), then the current $= \alpha m/1000 \cdot q\,(U+V)$. Since the potential difference between the sides of the cube is unity, the current (by OHM's law) is equal to the conductivity κ. Hence $\kappa = \alpha m/1000 \cdot q\,(U+V)$, or since $\Lambda = \kappa \cdot 1000/m$, we have, writing $u = q\mathrm{U}$, $v = q\mathrm{V}$, the equation $\Lambda = \alpha\,(u+v)$. Whilst U and V are the absolute velocities of the ions expressed in centims. per second, u and v are what are known as the "ionic mobilities" and are of the same dimensions as Λ.

The ionic velocities, and therefore also the ionic mobilities, are determined, not alone by the nature of the ion, but also by the solvent, the temperature, and the concentration of the solution. In considering the theory of ionisation it is customary to deal exclusively with the case of " dilute solutions" for which the values of the ionic mobilities do not differ appreciably from the values at infinite dilution, so that $u = u_\infty$, $v = v_\infty$ and $\dfrac{\Lambda}{\Lambda_\infty} = \alpha$ approximately.

This is the relation from which the coefficient of ionisation is usually deduced, but recent observations have shown that whilst the relation $\Lambda = \alpha\,(u+v)$ is universally true, the relation $\Lambda = \alpha\Lambda_\infty$ is only valid for solutions of concentrations below about N/100. At concentrations up to about decinormal it is probably legitimate to deduce the coefficient of ionisation from the osmotic constants of the solution or from the electromotive force of concentration cells (JAHN), but it is clear that, except in dilute solutions, the coefficients of ionisation and the ionic mobilities are altogether unknown quantities, and much confusion has arisen from the general tendency to

regard the ionic mobilities as constants for concentrated as well as for dilute solutions.

Correlation between Ionic Mobility and Fluidity.—The exact way in which the ionic mobility varies with the temperature and with the concentration of the solution is not known.

Without doubt the mobility depends chiefly upon the form and dimensions of the ions and the fluidity of the medium through which they travel. When the temperature or concentration of the solution is altered there is usually a marked alteration in its fluidity,* and the experimental data point to the conclusion that this produces a change in the ionic mobilities which may, as a first approximation, be justly regarded as proportional to the change of fluidity, so that $u = af$, $v = bf$ and $u+v = (a+b)f$, where f is the fluidity.

In certain cases this simple linear relationship undoubtedly exists. Thus, in the case of the excessively dilute solution which constitutes purified water, and in which the process of ionisation must be substantially complete, the conductivity is actually in direct proportion to the fluidity over the range of temperature from 0° C. to 36° C. (BOUSFIELD and LOWRY, *loc. cit.*, p. 48). KOHLRAUSCH has shown that the same relationship holds good in the case of dilute solutions of salts such as sodium valerate, in which the mobility of one of the ions is very small ('Roy. Soc. Proc.,' 1903, vol. 71, pp. 338–356). In other cases the linear relationship is less accurate, and although the ionic mobilities are closely related to the fluidity, they no longer obey a direct linear law. Thus KOHLRAUSCH ('Sitz. der Akad. Wiss. Berlin,' 1902, pp. 572–580) has shown that the temperature coefficients of ionic mobility in dilute solution are usually less than the fluidity coefficient, the greatest difference being found in the case of the mobile hydrogen and hydroxyl ions, for which the coefficients are 0·0154 and 0·0179 per degree Centigrade, as compared with 0·0254, for the conductivity and 0·0251 for the fluidity of water at 18° C. ; for the remaining ions the coefficients range from 0·0203 for the nitrate ion to 0·0261 for lithium. Furthermore, 'WOLF (' Zeit. Electrochem.,' 1902, pp. 117–119) and RUDORF ('Zeit. Phys. Chem.,' 1903, vol. 43, pp. 257–304) have shown that when the viscosity of a salt solution is increased at constant temperature by the addition of acetic acid or a non-electrolyte, the decrease of conductivity is proportionately less than the decrease of fluidity. It is, therefore, clear that the relation between mobility and fluidity is in general only approximately expressed by a linear law, but at present the necessary data are not available for any closer approximation to the form of the function. The linear law, which is an accurate expression in certain instances, we propose to use generally as a first approximation to the relationship between mobility and fluidity.

Intrinsic Conductivity.—The relations $\Lambda = \alpha(u+v)$, and $\Lambda_\infty = u_\infty+v_\infty$ being

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* In certain instances, and especially in the case of complex or hydrated ions, the dimensions of the ions may alter with the temperature and concentration of the solution, but usually this effect will be of secondary importance.

accurate, it follows that the true value of α for a given concentration and temperature is not $\alpha = \Lambda/\Lambda_\infty$, as is usually assumed, but

$$\alpha = \frac{\Lambda}{\Lambda_\infty} \cdot \frac{u_\infty + v_\infty}{u + v}.$$

That is to say, we must correct Λ for the change of mobility in order to arrive at the true value of α. The theoretical corrective factor for Λ is $\frac{u_\infty + v_\infty}{u + v}$, and we propose to call the product of Λ by this corrective factor the "intrinsic conductivity." It is the value of Λ reduced to the conditions of mobility which obtain at infinite dilution.

For practical purposes, and as a first approximation, we assume that

$$\frac{u_\infty + v_\infty}{u + v} = \frac{\text{fluidity at infinite dilution}}{\text{fluidity at given concentration}}.$$

Hence, taking the fluidity of the solvent (water) as unity and measuring the actual fluidity, f, at the given concentration in these units we have

$$\frac{u_\infty + v_\infty}{u + v} = \frac{1}{f}.$$

Denoting the intrinsic conductivity by I, we have, therefore, $I = \Lambda/f$, $I_\infty = \Lambda_\infty$, and hence $\alpha = I/I_\infty$. Whilst Λ/f does not represent the intrinsic conductivity as defined above with complete accuracy, it enables us to make a convenient practical approximation to the true value of α, which is much nearer than the current approximation $\alpha = \Lambda/\Lambda_\infty$.

The whole correction for changes of mobility is not large except in solutions of considerable concentration, so that any error in the correction applied will produce a much smaller error proportionately in the values deduced for the intrinsic conductivity and for the coefficient of ionisation. We believe, therefore, that by using the ratio $\alpha = I/I_\infty = \Lambda/\Lambda_\infty \cdot 1/f$, in place of the ratio $\alpha = \Lambda/\Lambda_\infty$, it will be possible to extend the method of determining α from conductivity measurements to solutions of considerably greater concentration than those for which the validity of the equation $\alpha = \Lambda/\Lambda_\infty$ can be recognised; and even in concentrated solutions the intrinsic conductivity deduced from the formula $I = \Lambda/f$ will enable a closer approximation to be made to the actual amount of ionisation than has been possible when this could only be deduced from the molecular conductivity of the solution.

Hitherto the majority of the conductivity measurements that have been made have been concerned with dilute solutions, in which the correction for viscosity is relatively small, but there is little doubt that when the necessary data of conductivity and viscosity are available for concentrated solutions, the study of the intrinsic conductivity of these solutions will lead to results at least as important as those derived from the study of dilute solutions. Unfortunately, the measurements that have been made of the viscosity of aqueous solutions, like those of the conductivity, have in almost every

case been restricted to dilute solutions, the data for the alkalies being even more scanty than those for acids and salts.* The only figures that we have been able to find are those of KANITZ ('Zeit. Phys. Chem.,' 1897, vol. 22, pp. 336–357), who gives the following table. No measurements appear to have been made in more concentrated solutions :—

Solution.	Viscosity.	Solution.	Viscosity.
NaOH N	1·2355	KOH 2N	1·2740
„ N/2	1·1087	„ N	1·1294
„ N/4	1·0560	„ N/2	1·0637
„ N/8	1·0302	„ N/4	1·0313
		„ N/8	1·0130

The results of our measurements, which were made by means of a new type of viscometer, which need not now be described, are set out in the following Table XIV., and are represented graphically in Diagram VIII. The relationship between the viscosity and the concentration can be expressed by the formula

$$\eta = 1 + 0{\cdot}199m - 0{\cdot}01833m^2 + 0{\cdot}01056m^3,$$

where m is the concentration in gram-molecules per litre, and the values derived from this formula are shown in column 5 of the table.

TABLE XIV.—Viscosity and Fluidity of Aqueous Solutions of Sodium Hydroxide at 18° C.

NaOH.	m.	H.	Viscosity.		δ.	Fluidity $f = \dfrac{1}{\eta}$.
			η (observed).	η (calculated).		
per cent. 0·0			1·0	1·0	±	1·0
2·50	0·64	86·4	1·08	1·12	0·04	0·923
7·68	2·08	26·7	1·43	1·43	±	0·700
14·28	4·15	13·35	2·25	2·27	0·02	0·444
20·14	6·13	8·82	3·84	3·96	0·12	0·260
25·0	7·94	6·67	6·69	6·72	0·03	0·145
30·2	10·03	5·14	11·81	11·81	±	0·0847
35·0	12·05	4·13	20·6	19·2	− 1·4	0·0485
40·0	14·29	3·34	32·3	30·9	− 1·4	0·0310
45·0	16·60	2·72	48·2	47·6	− 0·6	0·0207
50·6	19·37	2·17	74·7	74·7	±	0·0134

m = Concentration in gram-molecules per litre.

H = Hydration in molecules of water per molecule of sodium hydroxide.

* Data for the conductivity, density, and fluidity of solutions of sodium chloride from N/10 to 3N between 0° C. and 100° C. are given by LYLE and HOSKING (' Phil. Mag.,' 1902, vol. 3, 487–498).

On correcting the conductivities shown in Table XIII. for the changes of viscosity shown above, a series of values was obtained for the intrinsic conductivity, and these are shown in contrast with the values for the molecular conductivity in the last column of the same table. A graphical comparison of the two series of constants is given in Diagram IX. The values for the intrinsic conductivity show a remarkable *increase of conductivity in concentrated solutions* which is entirely masked in the specific and molecular conductivities. The minimum value occurs at about 8 per cent. NaOH, and in a 50-per cent. solution the intrinsic conductivity is nearly half as great again as in the most dilute solutions. This increase of conductivity we attribute to the fact that sodium hydroxide is an autolyte, that is to say, an electrolyte when fused, and may therefore be able in concentrated solutions to conduct the current quite independently of the ionising properties of the solvent.

Although it was obvious that the conductivity of concentrated aqueous salt solutions might be in part autolytic, we had hitherto been able to obtain no direct experimental evidence in support of this view. The case of sodium hydroxide is, however, especially favourable for the observations of this property, since its high solubility and low melting-point combine to produce in the concentrated solution a condition approximating unusually closely to that of the fused salt. Thus the minimum value in the intrinsic conductivity of zinc sulphate, to which attention has been called by SUTHERLAND ('Phil. Mag.,' 1902, VI., vol. 3, p. 171), is reached in a normal solution for which $I/I_\infty = 0.312$, but the measurements of conductivity and viscosity have only been carried as far as 5N, when the value of I/I_∞ rises to 0.443. This small increase in the intrinsic conductivity might conceivably have been due, not to the autolytic conductivity of the salt, but to some secondary cause, such for instance as over-correcting for the influence of viscosity. Such an explanation can scarcely be maintained in the case of sodium hydroxide, in which the value of I/I_∞, after falling to 0.0834 at 8 per cent. NaOH, rises again to 1.35 in a 50-per cent. solution.

These values apply to solutions at 18° C., a temperature at which the uncorrected specific and molecular conductivities give no indication of autolytic conductivity. As the temperature rises, however, the extreme viscosity of the concentrated solutions disappears, and the condition of the solutions approximates more and more to that of the fused salt, so that at 50° C. and 100° C. evidence of autolytic conductivity may be seen in the simple isothermal conductivity-concentration curves of Diagram XIII. These are described in Part VII. of the paper.

Clear indications having thus been obtained of autolytic conductivity in aqueous solutions of sodium hydroxide, it was not difficult to find other cases in which the abnormal properties of a solution could be referred to the same cause. This is notably the case with the solutions of zinc sulphate, ammonium sulphate and calcium chloride, for which SUTHERLAND found a minimum value of Λ/f. These minima were

not sufficiently pronounced to justify the unsupported assertion that their behaviour was due to the phenomenon now under discussion, but, when placed side by side with the curve showing the intrinsic conductivity of sodium hydroxide, the behaviour of these salts affords a striking confirmation of the view that the behaviour of sodium hydroxide is not unique, but is characteristic of the whole group of autolytes.

Owing to the great ionising power of water, the conductivity of dilute aqueous solutions is usually almost entirely heterolytic. With non-aqueous solvents it is often quite otherwise, and it is even possible that in certain cases the conductivity of the solution may be wholly autolytic. Thus it is stated that acetone and formic acid give conducting solutions of the autolytes KCl, KBr and KI, but not of the heterolytes HCl, and $CCl_3 \cdot CO_2H$ (see WALDEN and CENTNERSZWER, 'Zeit. Phys. Chem.,' 1902, vol. 39, p. 564), a result that is most easily explained by supposing that the acetone acts merely as a solvent, but is not able to bring about heterolytic conduction.

The task of distinguishing between autolytic and heterolytic conduction is greatly facilitated by the fact, which is brought out very clearly in the curve showing the intrinsic conductivity of sodium hydroxide at different concentrations, that whilst heterolytic conductivity rises to a maximum in the most dilute solutions, autolytic conductivity is greatest in the most concentrated solutions. The existence of autolytic conductivity affords, therefore, a simple explanation of the increase of molecular conductivity with concentration that has been not infrequently observed. Two examples of this kind were recorded by EULER ('Zeit. Phys. Chem.,' 1899, vol. 28, p. 622), who attributed the increase with concentration of the molecular conductivity of sodium bromide and iodide to the influence of the salt in increasing the ionising power of the solvent, that is, to an indirect, rather than to a direct, autolytic influence. In two of the cases recorded by KAHLENBERG ('Journ. Phys. Chem.,' 1903, vol. 7, pp. 254–258) the molecular conductivity (of silver nitrate and of ferric chloride in amylamine) did not increase continuously with the concentration, but reached a maximum and then decreased; it is clear, however, that in these solutions the final decrease of molecular conductivity may be attributed to the great viscosity of the concentrated solutions, to which reference is made in the paper. It is of interest to note that KABLUKOFF ('Phys. Chem.,' 1889, vol. 4, p. 429) noticed an increase with concentration in the molecular conductivity of hydrogen chloride dissolved in ether; this may perhaps be attributed to the autolytic conductivity of the oxonium salt $\begin{smallmatrix} C_2H_5 \\ C_2H_5 \end{smallmatrix}\!\!>\!\!O\!\!<\!\!\begin{smallmatrix} H \\ Cl \end{smallmatrix}$. Similar observations have been made more recently by McINTOSH and ARCHIBALD ('Roy. Soc. Proc.,' 1904, vol. 73, pp. 454–455) and by J. W. WALKER ('Trans. Chem. Soc.,' 1904, vol. 85, pp. 1082–1098).

PART VII.—INFLUENCE OF TEMPERATURE ON THE CONDUCTIVITY OF AQUEOUS SOLUTIONS OF SODIUM HYDROXIDE.

Amongst the earliest investigations of the influence of temperature on conductivity is that of KOHLRAUSCH ('Wied. Ann.,' 1879, vol. 6, pp. 1 and 145 ; 1885, vol. 26, p. 161), who measured the linear temperature coefficients of most of the solutions examined, and in several cases determined also the coefficient of t^2 in the equation $\kappa_t = \kappa_0 (1 + \alpha t + \beta t^2)$. He found that the salts gave positive values for β, and the acids negative values. A dilute solution of sodium hydroxide gave a very small positive coefficient, the relationship between temperature and conductivity being very nearly linear over the range of temperature studied. Subsequent investigations have been made by ARRHENIUS, who discovered that the coefficients for phosphoric and hypophosphous acids become negative above 54° C. and 75° C. respectively, so that the conductivity actually reaches a maximum value, whilst SACH, HOLLAND, and TROTSCH ('Ann. Phys. Chem.,' 1890, III., vol. 41, pp. 259–287) showed that the curves for certain sulphates and for the chlorides of copper and cobalt were inflected at the higher temperatures, a supposed abnormality which they attributed to loss of water of crystallisation by the dissolved salts. A detailed bibliography of temperature-conductivity measurements is given by KOHLRAUSCH and HOLBORN ('Leitvermögen,' pp. 145–158, 195–199).

The first indication of any general law governing the temperature coefficients of electrolytic conductivity was obtained by KOHLRAUSCH ('Sitz. Preuss. Akad. Wiss.,' 1901, vol. 42, p. 1026), who found that in the case of the most dilute solutions, and within the somewhat narrow range of temperatures investigated, the two coefficients in the formula

$$\kappa_t = \kappa_{18} \{1 + \alpha (t - 18) + \beta (t - 18)^2\}$$

were related to one another by the simple equation $\beta = 0.0163 (\alpha - 0.0174)$. In this way it was shown that if α were known, the value of β could be deduced without any further experimental observations, so that between 2° C. and 34° C. the whole influence of temperature on conductivity could be expressed by means of a single arbitrary constant. The relationship between the coefficients may be expressed almost equally well by the equation $\beta = \frac{1}{57} \{\alpha - \frac{1}{57}\}$, and when this value for β is substituted in the equation for κ_t, it is seen that κ_t becomes zero when $t - 18 = -57$, whatever the value of α, in other words, the whole of the parabolic conductivity-temperature curves must, if produced (without taking account of change of the constants), converge to a common point on the axis of temperature, situated at 57° − 18° = 39° C. below the freezing-point of water. This point has been named the "conductivity-zero" for water, and the most remarkable observation recorded in KOHLRAUSCH's paper is to the effect that the viscosity of water also extrapolates to a limiting value at this point. It was thus evident that the common factor determining

the convergence of the conductivity-temperature curves was simply the viscosity of the solvent. We are indebted to Dr. LARMOR for the suggestion that this result may be indicated by factorising the equation $\kappa_t = \kappa_0 (1 + \alpha t + \beta t^2)$ and writing it in the form $\kappa_t = \kappa_0 (1 + at)(1 + bt)$, where a is a coefficient depending on the (viscosity of the) solvent, whilst b is a specific constant of the electrolyte under consideration, both a and b, however, being constant only over a narrow range of temperature.

A fuller study of the influence of temperature on the conductivity of composite electrolytes led to the conclusion that it was possible to represent all the experimental data by means of a generalised conductivity-temperature curve having the form shown in fig. 6 (BOUSFIELD and LOWRY, *loc. cit.*, p. 52). The most important
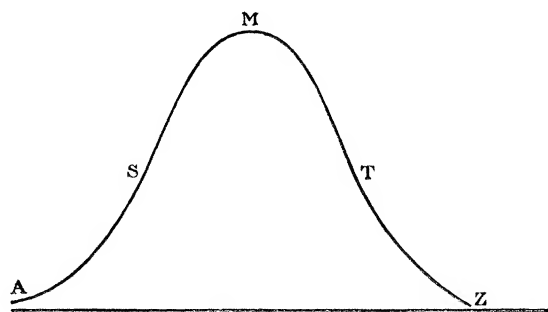
Fig. 6.

features of this curve are (1) a more or less tangential approach A to the axis of temperature, (2) a point of inflexion S, (3) a maximum conductivity at M, and (4) a rapid fall almost to zero in the neighbourhood of the critical temperature Z of the solution, with possibly a second point of inflexion T. In addition to the evidence brought forward at the time, confirmation of this view has been afforded by the measurements by KUNZ ('Comptes Rendus,' 1902, vol. 105, p. 788; 'Zeit. Phys. Chem.,' 1903, vol. 42, pp. 591–596) of over-cooled aqueous solutions, which show that the conductivity-temperature curves, instead of cutting the axis of temperature as is indicated by the parabolic formula $\kappa_t = \kappa_0 (1 + \alpha t + \beta t^2)$, approach it nearly tangentially; in the other direction, NOYES and COOLIDGE ('Zeit. Phys. Chem.,' 1903, Jubelband, p. 372), working with aqueous solutions under high pressures, have shown that even powerful electrolytes like sodium and potassium chlorides reach a maximum conductivity at high temperatures; in decinormal solutions this occurs at about 280° C., and above that temperature these salts exhibit negative coefficients. As regards non-aqueous solutions, the measurements by EVERSHEIM ('Ann. Physik,' 1904, iii., vol. 13, pp. 492–511) of the conductivity of liquid ammonia, of ammonia containing 1 per cent. of copper nitrate, and of sulphur dioxide, have yielded additional evidence of the correctness of the curve at the upper temperature limits of conductivity.

The original object of the investigation described below was to obtain evidence of the correctness of our view that the point of inflexion S was a normal feature of the

conductivity-temperature curves, and not the product of some abnormal change in the character of the solution. A series of measurements, made some years ago, had shown that dilute solutions of the alkalies gave inflected curves. As there was no reason to suspect the existence of any special complications in the case of such simple substances, the conditions appeared to be particularly favourable for the investigation of the nature of the point of inflexion and its dependence on the character of the alkali and the concentration of the solution. The experiments now described deal exclusively with sodium hydroxide, but the few measurements that we have made with other alkalies have shown that they all behave in a similar manner, as indeed had been indicated by our earlier observations.

Turning now to the specific case of sodium hydroxide, it may be noted that although the linear temperature coefficient of conductivity has frequently been noted, very few measurements have been made of its variation with temperature. KOHLRAUSCH (*loc. cit.*, 1885) investigated solutions containing 2·61 per cent. and 42·7 per cent. NaOH and gave the formulæ

$$\text{NaOH } 2\text{·}61 \text{ per cent. } \kappa_t = 680\,(1 + 0\text{·}0295t + 0\text{·}0000016t^2)$$
$$\text{,, } \quad 42\text{·}7 \quad \text{,, } \quad \kappa_t = 240\,(1 + 0\text{·}0866t + 0\text{·}004511t^2).$$

He also noticed the great increase of conductivity with temperature in the case of the more concentrated solutions, and recorded an increase of 100-fold in the conductivity of a 40-per cent. solution between $-10°$ C. and $+80°$ C. His figures are given below.

T.	k (observed).	k (calculated).	δ.
° C.			
− 9·30	87	89	2
+ 0·07	250	224	− 26
+18·04	958	968	+ 10
+42·9	3072	3052	− 20
+79·1	8214	8275	+ 61

The calculated values in this table are derived from the parabolic formula

$$\kappa_t = 222\,(1 + 0\text{·}01059t + 0\text{·}004459t^2).$$

In neither case did the observations come within the range within which a point of inflexion may occur. DÉGUISNE (' Dissertation, Strassburg,' 1895), working between 2° C. and 34° C., was also able to represent his measurements of the alkalies by means of a flat parabola, and the existence of a point of inflexion in these curves appears hitherto to have been entirely overlooked. This result is largely to be attributed to the fact that the point of inflexion for solutions of caustic soda never falls much below 50° C. and recedes above 100° C. both in dilute and in concentrated solutions, and also to the fact that a parabolic curve has been assumed to express universally the temperature-conductivity relation.

Experimental Methods.

(1.) *The Glass Vessels.*—In measuring the temperature coefficients of conductivity the two chief difficulties were (1) the exact regulation of the temperature in the higher ranges, and (2) the fouling of the solutions by the action of the glass of the conductivity vessels. The earlier observations were made in glass vessels of the form shown in fig. 7 ; the resistance capacity, which was dependent upon the length and diameter of the U-tube between the electrodes, was measured with the help of the
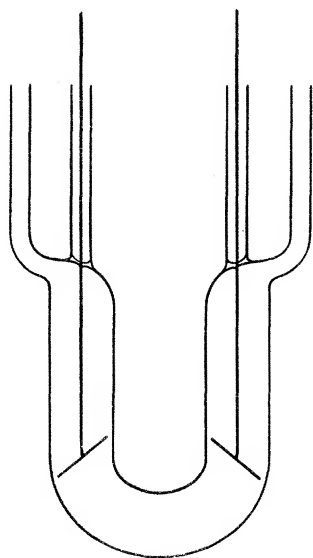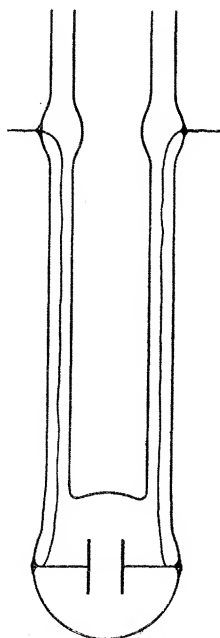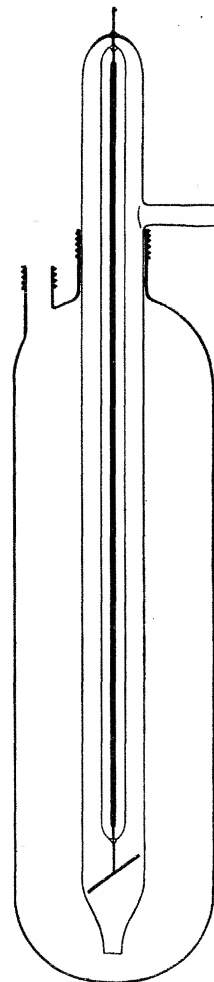
Fig. 7.   Fig. 8.   Fig. 9.

standard solutions recommended by Kohlrausch, Holborn and Diesselhorst ('Wied. Ann.,' vol. 64, pp. 440 and 451, 1898) ; the capacities of the vessels used were as follows : L_2, 2·156 cm.$^{-1}$; L_4, 4·125 cm.$^{-1}$; L_{13}, 13·36 cm.$^{-1}$; L_{54}, 54·73 cm.$^{-1}$; L_{162}, 162·62 cm.$^{-1}$. For the lower capacities the U-vessel was modified, as shown in fig. 8 ; a vessel of this type was used for the more dilute solutions and had the capacity $N_{0·1}$, 0·1236 cm.$^{-1}$.

(2.) *Adjustment of Temperature.*—These glass vessels were placed in a large water-bath, holding about 100 lbs. of water, and the conductivity was measured at

intervals of 20° C. on the ascending scale and 10° C. on the descending scale of temperatures. It was found that under these conditions the heating and cooling occupied almost exactly the same period of time, and we were therefore able to apply a simple correction for the loss* of conductivity due to the neutralisation of the alkali by the silica of the glass, by assuming that the fouling took place to an equal extent during the periods of heating and cooling. The temperatures were measured by means of a pair of thermometers graduated in tenths on an open scale and reading from 0° C. to 50° C. and from 50° C. to 100° C.; these thermometers had been recently calibrated at the Reichsanstalt, Charlottenburg, and the errors were known within 0·01° C. In the lower ranges an exact adjustment of temperature was possible, but in the higher ranges it was not found possible to avoid fluctuations of several hundredths on either side of the steady temperature at which it was desired to determine the conductivity.

(3.) *Determination of Temperature Coefficients with the Help of Platinum Apparatus.*—During the later part of the investigation we had at our disposal a silver-encased platinum bottle of about .500 cub. centims. capacity, in which we were able to carry out conductivity measurements between 0° C. and 100° C. without appreciable fouling of the solutions. The bottle and the electrodes used with it had the form shown in fig. 9. The resistance capacity was dependent upon the form of the glass tube surrounding the inner electrode; the electrodes principally used for this series of observations had the capacities 16·371 and 3·293 cm.$^{-1}$. The area of glass was much less than in the electrode designed for measurements at 18° C., and the electrode was lifted out of the solution and allowed to drain when not actually in use. The solution within the tubes was displaced from time to time by forcing air free from carbon dioxide through the side tube of the electrode. The smaller neck of the bottle was used to admit a thermometer, by which the actual temperature of the solution could be determined; the four thermometers used for this purpose were graduated in tenths from 0° C. to 25° C., 25° C. to 50° C., 50° C. to 75° C. and 75° C. to 100° C., and had recently been calibrated at the Reichs-anstalt, the errors being given to 0·02° C. at the lower and 0·05° C. at the higher temperatures. The platinum pot, described in Part. I. of the paper, was also used in a modified form for some of the latest temperature-conductivity measurements. In these measurements the solution was initially heated to 100° C., and the conductivity determined at a series of temperatures from 100° C. to 0° C.; the density of the solution was then determined and its exact concentration deduced; any change of concentrations that might have been produced by the distillation of water from the solution during the initial heating was thus allowed for.

(4.) *Accuracy of the Observations.*—As has already been pointed out, the chief errors in determining the temperature coefficients of conductivity are (1) those due to temperature adjustment, and (2) those due to fouling of the solutions, but in

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* The most dilute solutions gained in conductivity by the dissolution of the glass.

addition to these definite sources of error the whole operation of measuring the conductivity becomes troublesome when the temperature is raised, and it is therefore not possible to work with the same exactitude as at lower temperatures, at which the distraction and haste arising from temperature adjustment is absent.

In dilute solutions, for which the temperature coefficient $\kappa^{-1}d\kappa/dt$ is about 2 per cent., an error of $0.05°$ C. in the temperature produces an error of 0.1 per cent. in the conductivity, but in the concentrated solutions the temperature coefficients are enormously greater. The conductivity of a 50-per cent. solution instead of increasing in the ratio of $7:2$ between $0°$ C. and $100°$ C. actually increases 5-fold between $0°$ C. and $18°$ C., and 80-fold between $0°$ C. and $100°$ C. For this reason we are unable to claim for our individual measurements at the higher temperatures an accuracy greater than about 1 part in 100, though the error on a series of measurements may be considerably less.

The total change of conductivity due to the fouling of the solutions heated and cooled in glass vessels amounted in two instances to as much as 1.6 per cent., but the greater part of this is eliminated by our method of correction, and the residual error can scarcely amount to more than 0.5 per cent., since the total change in either the ascending or the descending series cannot have differed much from the half-value, 0.8 per cent., that was taken as the basis of our calculations. When using platinum vessels this source of error was eliminated, but the results obtained were so similar in their general character to those obtained when using glass vessels, that we did not consider it necessary to repeat all our observations in order to secure the increase of accuracy that might have resulted from the removal of only one of the sources of error.

TABLE XV.—Influence of Temperature on Conductivity.

P.	$m.$	$\kappa_0.$	$\kappa_{18}.$	$\kappa_{50}.$	$\kappa_{100}.$	$K_0 = \dfrac{\Lambda_0}{\Lambda_{18}}.$	$K_{50} = \dfrac{\Lambda_{50}}{\Lambda_{18}}.$	$K_{100} = \dfrac{\Lambda_{100}}{\Lambda_{18}}.$	Temperature of inflexion.
49·68	18·90	(0·01775)	(0·0830)	(0·3918)	(1·283)	0·2119	4·781	16·06	—
46·74	17·46	0·02168	0·09235	0·4081	1·294	0·2328	4·478	14·54	—
43·56	15·94	0·02656	0·10384	0·4286	1·319	0·2536	4·192	13·22	—
40·40	14·47	(0·03349)	(0·1181)	(0·4503)	(1·340)	0·2821	3·871	11·80	—
39·72	14·17	0·03590	0·12245	0·4559	1·348	0·2907	3·781	11·46	—
34·43	11·82	(0·05728)	(0·1613)	(0·5157)	(1·385)	0·3522	3·246	1·947	—
29·76	9·855	0·08873	0·2114	0·5798	1·408	0·4163	2·781	6·941	—
26·68	8·615	(0·1147)	(0·2494)	(0·6255)	(1·411)	0·4563	2·546	5·895	—
19·96	6·078	0·1810	0·3272	0·6776	1·325	0·5490	2·102	4·222	91°
14·96	4·349	0·2106	0·3493	0·6505	1·159	0·5985	1·890	3·460	82
10·56	3·058	(0·2020)	(0·3175)	(0·5601)	(0·9246)	0·6322	1·773	3·035	74
3·85	1·000	(0·1047)	(0·1575)	(0·2600)	(0·4068)	0·6618	1·671	2·693	48

NOTE.—The values for κ_0, κ_{18}, κ_{50}, and κ_{100} which are enclosed in brackets are derived from conductivity-temperature observations in vessels that had not been independently calibrated; values of κ_{18} were taken from the isothermal observations recorded in Table XII., the concentration of the solutions being deduced from their densities at $18°$ C.; the values of κ_0, κ_{50}, and κ_{100} were then calculated from the ratios K_0, K_{50}, K_{100} tabulated above.

EXPERIMENTAL RESULTS.

The general nature of the experimental results may be indicated by giving conductivity-temperature curves for two different concentrations. In Diagram X. are given (1) a curve showing the influence of temperature on the molecular conductivity of a normal (4-per cent.) solution; this curve shows a well-marked point of inflexion at 48° C.,* and is typical of the curves for moderate dilution. (2) A similar curve for a 40-per cent. solution, which is not inflected between 0° C. and 100° C., and may be regarded as typical of the behaviour of concentrated solutions. The data on which these curves are based are shown in Table XIX., p. 305.

The variation of the temperature of inflexion with the concentration of the solution is shown in Table XV. and Diagram XI., and presents some interesting features. The minimum value for the temperature of inflexion is at 48° C. in a normal solution, but a rapid rise occurs as the concentration is increased, and at 25 per cent. NaOH (8·5 N) the inflexion has risen to 100° C.; above this concentration the inflexion is no longer observed between 0° C. and 100° C., but the formulæ described below indicate that even at the highest concentrations the temperature of inflexion is only a few degrees above 100° C. The most dilute solutions also appear to give curves which are not inflected, but we are unable at present to supply definite data with reference to the variations in the temperature of inflexion at concentrations below normal.

In explanation of the great variations in the character of the conductivity-temperature curves, it should be recalled that the point of inflexion is in the neighbourhood where the increase of conductivity due to increasing fluidity begins to be overbalanced by the diminution of conductivity due to decay of ionisation with rising temperature. Now in the most dilute solutions " ionisation " is nearly complete, and, as the coefficient of ionisation is thus not greatly influenced by temperature, the form of the curve is determined mainly by changes in the viscosity of the solution. So also in the most concentrated solutions the alterations of viscosity are so great that any changes in the coefficient of ionisation are only of secondary importance. It is, therefore, only at intermediate dilutions that the point of inflexion can be observed at temperatures between 0° C. and 100° C.

Another way of showing the great difference in the influence of temperature on the conductivity of concentrated and dilute solutions is by calculating the ratios K_0, K_{50} and K_{100} of the conductivities at 0° C., 50° C. and 100° C. to those at 18° C; in Table XV the ratio given is that of the molecular conductivities, since a correction has been introduced for the alteration of volume-concentration produced by the contraction or expansion of the solution. The figures given in the table are plotted in Diagram XIV., and indicate very clearly the more important characteristics of the different solutions.

Having determined the temperature coefficients for a considerable range of dilutions,

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* In the curve showing the influence of temperature on the *specific* conductivity (compare Table XVII., p. 303) the inflexion is at 44° C.

it was of interest to determine the character of the change produced by alterations of temperature in the isothermal conductivity-concentration curve of Diagram VII. The curves for 0° C., 18° C., 50° C., and 100° C. are shown in Diagram XIII., and the data are tabulated in Table XV. The most striking features are :

(1.) The great increase in the maximum specific conductivity and the gradual shifting of the maximum in the direction of the more concentrated solutions; this is shown in Table XVI.

TABLE XVI.

Temperature.	Maximum conductivity.	Percentage at which maximum occurs.	Conductivity of 49·68-per cent. solution.	Percentage of maximum conductivity.
° C. 0	0·214	13	0·01175	5·50
18	0·3490	15	0·0830	23·8
50	0·674	19	0·3198	47·4
100	1·410	27	1·283	83·8

(2.) A remarkable holding up of the conductivity of the most concentrated solutions. Thus the conductivity of a 50-per cent. solution at 0° C. is 5 per cent. of the maximum, at 18° C. 24 per cent., at 50° C. 47 per cent., and at 100° C. 84 per cent.

(3.) It is noteworthy that the isothermal curves for 50° C. and 100° C. give clear indications that at these temperatures liquid (over-cooled) sodium hydroxide would possess a very considerable conductivity. The power to conduct in the fused state is necessary, in order to explain the form of the two isothermal curves referred to, and the fact that this effect can already be detected in solutions containing less than 50 per cent. NaOH affords very strong confirmatory evidence of the view arrived at from the study of the intrinsic conductivity in Part VI. of the paper, that in concentrated aqueous solutions the conductivity of sodium hydroxide is to a large extent independent of the ionising power of the solvent, and depends on the self-ionising properties of the liquid alkali. If reference be made to the curves in Diagram XIII., it will be seen that whilst the curve for 0° C. leads down almost to zero value for the conductivity at concentrations above 50 per cent. NaOH, the curves for 50° C. and 100° C. cannot be brought down to the axis of concentration, except by introducing an additional point of inflexion in the curve, which there is no reason to suppose exists.

Form of the Curves. Cubic Formula.—Hitherto the conductivity-temperature relations have been expressed exclusively by linear or parabolic formulæ, but these are obviously incapable of representing a curve containing a point of inflexion. The normal solution of sodium hydroxide, which shows the inflexion very clearly, formed the starting-point of the investigation of the form of the curves which is now described. The series of values given in Table XVII. having been obtained, a curve was plotted of the approximate values of $d\kappa/dt$ at different temperatures obtained by

subtracting consecutive values of κ and dividing by the temperature differences. The curve so plotted was obviously a parabola with axis at right angles to the axis of temperature and vertex at the value of $t = 44°$ approximately. The equation of this parabola was of the form

$$dκ/dt = a - b\,(44-t)^2,$$

which, on integration, gave the conductivity-temperature relation in the form of a simple cubic equation

$$\kappa = c + \alpha t + \gamma\,(44-t)^3.$$

The values of the constants worked out at $c = 0\cdot0980$, $\alpha = 0\cdot00321$, $\gamma = 0\cdot0000000767$; using these constants, the calculated values shown in the table were obtained. As will be seen, they agree with the observed values within the limits of experimental error.

TABLE XVII.

$t.$	κ (observed).	κ (calculated).	Difference.
0·30	0·1048	0·1045	− 3
14·71	0·1467	0·1471	+ 4
18·00	0·1571	0·1571	±
29·1	0·1917	0·1917	±
40·65	0·2285	0·2285	±
49·65	0·2574	0·2574	±
59·55	0·2888	0·2889	+ 1
71·37	0·3255	0·3255	±
89·11	0·3767	0·3770	+ 3
99·5	0·4046	0·4043	− 3

Significant Formula for the Conductivity-Temperature Curves.—The cubic formula gave a satisfactory agreement in the case of those curves which exhibit a point of inflexion between 0° C. and 100° C., but was not so satisfactory when applied to curves which are not inflected between these limits. We were, therefore, led to devise a formula which should give expression to the variation with temperature of the three factors of concentration, ionic mobility and ionisation, on which the specific conductivity depends. Of these only one can be directly determined, namely, the concentration, which decreases with rising temperature in the same ratio of the density.

In arriving at the significant formula we have assumed, in accordance with the considerations advanced in Part VI. of the paper, that the changes of ionic mobility may be expressed by a formula similar to that which represents the influence of temperature on fluidity, an assumption which does not depend on the existence of any direct proportionality between mobility and fluidity. In a similar manner we have assumed that the decay of ionisation may be expressed by a formula similar to that which represents the decrease of specific inductive capacity with rising temperature.

This assumption, also, does not postulate any direct proportionality between the two quantities, but is sufficiently justified by the general relationships to which J. J. THOMSON and NERNST have called attention.

In order to express the variations of ionic mobility we have made use of SLOTTE's fluidity formula:

$$f = \eta^{-1} = c\,(1+bt)^n$$

where η is viscosity, t is temperature, nbc are constants, the general applicability of which has been fully demonstrated by THORPE and RODGER in their Bakerian Lecture ('Phil. Trans.,' A, 1894, vol. 185, pp. 397–710). To express the variations of ionisation we have adopted the formula

$$D = ce^{-at},$$

which is used by ABEGG and SEITZ to express the relation between the dielectric constant D and the temperature t for a series of alcohols ('Zeit. Phys. Chem.,' 1899, vol. 29, p. 242), and which we find to be applicable also to EVERSHEIM's values for the dielectric constant of sulphur dioxide almost up to the critical temperature. Combining these formulæ with that given in Part VI. for the specific conductivity,

$$\kappa = \frac{\alpha m}{1000}\,(u+v),$$

we get the relation

$$\frac{\kappa_t}{\kappa_0} = \frac{\rho_t}{\rho_0}\,(1+bt)^n\,10^{-at}$$

for the variations of specific conductivity with temperature, and for the variations of molecular conductivity

$$\Lambda_t/\Lambda_0 = (1+bt)^n\,10^{-at}.$$

It is to be noted that the formulæ thus deduced have an empirical value which is independent of the theoretical consideration that led to their construction.

For the purpose of expressing and tabulating the experimental results it was convenient to correct at once for the measured variations of concentration and to work with the molecular rather than with the specific conductivity. It was further convenient for the purpose of comparing the influence of temperature on the conductivity of solutions of different concentrations to refer the molecular conductivities to those at 18° C. as unity and to tabulate only the ratios

$$K_0 = \Lambda_0/\Lambda_{18}, \qquad K_{50} = \Lambda_{50}/\Lambda_{18}, \qquad K_{100} = \Lambda_{100}/\Lambda_{18}, \ \&c.$$

The exponential factors in the equations given above have been taken to base 10, and the form generally employed for arithmetical computation was

$$\log_{10} K = \log_{10} K_0 + n\log(1+bt) - at.$$

Experimental Verification of the Significant Formula.—In order to test the validity of the formula, two solutions of widely differing concentrations were taken : a normal solution and solution of 40·4 per cent. strength. The approximate values of the expression $\kappa^{-1} d\kappa/dt$ were plotted out against temperature and gave the form of a rectangular hyperbola. This is the relation which we get at once by differentiating the above equation, and it may be written in the form

$$\left(\frac{1}{\kappa} \cdot \frac{d\kappa}{dt} + \frac{a}{\mu}\right)\left(t + \frac{1}{b}\right) = n.$$

In the two sets of results given below the values of the constants were obtained from this hyperbola, but subsequently a more convenient method for calculating them was devised.

The constants so obtained were :—

For normal solution

$$a = 0{\cdot}003182, \quad b = 0{\cdot}01356, \quad n = 2{\cdot}493.$$

For 40·4-per cent. solution

$$a = 0{\cdot}00603, \quad b = 0{\cdot}0248, \quad n = 4{\cdot}107.$$

Using these constants to calculate the values of K, we obtain the results which are shown in the subjoined Table XVIII. and in Diagram XII. in comparison with the observed results.

TABLE XVIII.

Normal solution.				40·4-per cent. solution.			
Tempera-ture.	K (observed).	K (calculated).	Difference.	Tempera-ture.	K (observed).	K (calculated).	Difference.
0·8	·6759	·6759	±	0·76	·3004	·3013	+ 9
5·0	·7519	·7514	− 5	4·97	·4235	·4242	+ 7
10·4	·8531	·8539	+ 8	10·38	·6248	·6254	+ 6
18·0	1·000	1·003	+ 3	18·0	1·000	1·000	±
29·1	1·226	1·228	+ 2	29·1	1·760	1·754	− 6
40·05	1·453	1·455	+ 2	40·05	2·762	2·748	− 14
50·15	1·674	1·671	− 3	50·15	3·889	3·884	− 5
59·91	1·875	1·879	+ 4	59·91	5·176	5·166	− 10
71·37	2·121	2·121	±	69·94	6·651	6·649	− 2
80·00	2·303	2·299	− 4	80·00	8·276	8·277	+ 1
89·89	2·496	2·498	+ 2	89·89	9·960	9·978	+ 18
100·2	2·697	2·697	±	100·2	11·84	11·83	− 1

Having regard to the method adopted for calculating the constants, and to the experimental errors introduced by the use of glass vessels, the agreement appears to to be sufficiently close to demonstrate the general validity of the relation.

We were thus enabled, for the first time as we believe, to express the relation between the temperature and conductivity of an electrolyte in terms which exhibit the separate effect of the two main factors involved, namely, change of viscosity and change of ionisation.

It now remained to determine the variation of the coefficients over the whole range of concentrations. In the present communication we have been obliged to limit our observations to the range of concentrations from 50 per cent. down to 4 per cent. (normal), but we hope at some future time to resume the investigation of the more dilute solutions, which promise to yield results at least equal in importance to those derived from the study of the more concentrated solutions. The values of the coefficients are somewhat irregular if derived either by the method described above or by calculation from four particular observations of any series, since small experimental errors might produce much larger errors in the values of the coefficients. The points chosen for the initial computation of the coefficients were the experimental values for K_0, K_{50} and K_{100} for each of the concentrations studied. On plotting out the values so obtained it appeared that the values for a and n could be very simply expressed in terms of the concentration. The relation of n to the concentration m of the solution was $n = 1\cdot910 + \log_{10}(m + 0\cdot654)^2$, and we were able to adjust the constants in this expression so that when $m = 0$, $n = 1\cdot542$, the index given by THORPE and RODGER for the index n in SLOTTE's formula for the fluidity of water. This relation, we have reason to believe, holds good right through the range of dilute solutions down to water.

From 50 per cent. nearly down to normal the coefficient a is related in a linear manner to the concentration m, a result that may be expressed by means of the equation $a = 0\cdot00293 + \frac{1}{4000}m$. In the case of "water" we have reason to believe that there is no appreciable "decay of ionisation" between $0°$ C. and $100°$ C., so that when $m = 0$ we should have $a = 0$. The rapid drop in the value of a, which actually occurs below normal concentration, is not expressed by the above linear relationship, and we have provisionally added a small term to the linear equation, which is then made to read $a = 0\cdot00293 + \frac{1}{4000}m - 0\cdot000146/(m + \frac{1}{20})$. The effect of this added term is to make $a = 0$ when $m = 0$. We believe that further investigation will justify some such addition, which hardly affects the figures for concentrations above normal, and which corresponds roughly to the facts indicated by our incomplete experiments on dilute solutions.

Having thus determined the relations of n and a to the concentration from a study of all the individual values for K_0, K_{50}, K_{100}, we now took the smooth values for n and a given by the above expressions, and recalculated the values of b from the equation $\log K = \log K_0 + n \log(1 + bt) - at$, by substituting the experimental values of K_{100} and K_0, and the smooth values for n and a. The same process was repeated using the experimental values of K_{50} in place of those of K_{100}. In this way all the errors of observation, whether from inaccurate reading or fouling of solutions or determina-

tion of density and concentration, together with any errors in the adjustment of the constants for a and n, are thrown upon the coefficient b. The accuracy of the experimental work, and the validity of the formula for the influence of temperature on conductivity, can then be tested (1) by comparing the two values of b deduced from K_{50}, K_{100} respectively (Table XIX.), (2) by the smoothness or otherwise of the curve representing the variation of b with the concentration of the solution (Diagram XIV.).

In Table XIX. are given the values of the coefficients for all the solutions referred to in Table XV. The values of a and n are the values derived from the expressions formulated above. The values for b are those derived from K_{100} and K_{50}. It will be observed that in the column of differences for the b values, there is a progressive series of positive differences followed by a series of negative differences. This is mainly due to the fact that the slope of the line representing the variation with concentration of the constant a was chosen so as to give the values for a at 40 per cent. and at 4 per cent as close as possible to these individual values. A closer agreement would have resulted if the linear relationship had been adjusted for 40 per cent. and 10 per cent., but the differences were so small that it was not deemed necessary to repeat the somewhat tedious calculations involved. The values of the constants are plotted out in Diagram XIV., and the smoothness of the individual values for b is a satisfactory indication of the validity of the formula employed.

TABLE XIX.—Coefficients in the Equation

$$K = K_0 \, 10^{-at} (1 + bt)^n.$$

P.	m_{18}.	$a \times 10^5$.	n.	b from K_{100}.	b from K_{50}.	b Differ-ence.	$T = \dfrac{1}{b}$.	θ_1.	θ_2.
								° C.	° C.
0·0	0·0	0	1·542	·0269	·0277				
3·85	1·000	304	2·347	·01450	·01446	− 4	− 69·06	48	
10·56	3·058	362	3·049	·01200	·01216	+16	− 82·10	74	493
14·96	4·349	397	3·308	·01241	·01254	+13	− 80·16	82	480
19·96	6·078	443	3·566	·01359	·01362	+ 3	− 73·45	91	462
26·68	8·615	506	3·844	·01635	·01652	+17	− 60·85	101	438
29·76	9·855	538	3·953	·01788	·01784	− 4	− 55·99	103	423
34·43	11·82	589	4·102	·02063	·02054	− 9	− 48·58	105	403
39·72	14·17	647	4·252	·02369	·02356	−13	− 42·30	105	381
40·40	14·47	655	4·269	·02416	·02410	− 6	− 41·44	105	379
43·56	15·94	692	4·350	·02579	·02578	− 1	− 38·78	103	365
46·74	17·46	730	4·426	·02712	·02716	− 5	− 36·79	101	351
49·68	18·90	765	4·492	·02879	·02872	− 7	− 34·78	100	341

Physical Meaning of the Coefficients.—The formula used to represent the influence of temperature on conductivity is of value not only because it gives us an exact

representation of the different types of conductivity-temperature curve, but also because a definite physical meaning can be assigned to each of the coefficients. Moreover, the formula has a special value because it renders it possible more or less accurately to resolve the two opposing influences to which the conductivity-temperature curves owe their peculiar form. Although it is not possible to test, by direct experiment, the accuracy or otherwise of the constants which we have deduced for the temperature variations of the coefficient of ionisation and the ionic mobilities, the constants are of the right order of magnitude for the physical properties which they are intended to represent.

Thus the constant n, which we may term the index of mobility, varies from $1\cdot5$ for water to $4\cdot5$ for a 50-per cent. solution of sodium hydroxide. Although these values were deduced entirely from electrical measurements, it was expected that they would be comparable with the indices in SLOTTE's viscosity formula, and the values of n, given in Table XIX., cover almost the whole range of variation of this constant in the viscosity measurements of THORPE and RODGER. A high constant represents a rapid decrease of viscosity, and may usually be attributed to rapid depolymerisation of the liquid. It is noteworthy that values of n, comparable with those given in our table for concentrated solutions of sodium hydroxide, were observed only in the case of the alcohols : ethyl alcohol, $n = 4\cdot37$; isopropyl alcohol, $n = 4\cdot9$ to $3\cdot4$; amyl alcohol, $n = 4\cdot3$; all of which are known to exist largely in the form of complex molecules.

The constant b is related by the expression $b = 1/\mathrm{T}$ to the "conductivity zero" T of the solution (BOUSFIELD and LOWRY, $loc.\ cit.$, p. 44), and although this zero does not represent an actual physical fact, it gives a valuable mental picture of the way in which the increase of viscosity at low temperatures tends to destroy the conductivity of the solution. The values of T are given in the eighth column of Table XIX., and correspond closely with the conductivity zeros deduced from a simple parabolic formula for the influence of temperature on conductivity.

The constant a, tabulated in the third column of Table XIX., measures the rate of decay of ionisation with rising temperature, and is greatest in the most concentrated solutions.

Points of Inflexion.—The above expression for the influence of temperature on conductivity enables us to calculate the positions of both the points of inflexion and the maximum of conductivity of our general curve. The results are given in Table XIX., which shows under θ_1 and θ_2 the temperatures corresponding to the lower and upper points of inflexion in the curve of molecular conductivity, whilst the temperature of maximum conductivity is given by $\frac{1}{2}(\theta_1+\theta_2)$. The values of θ_1, occurring as they do within or close to the experimental range of temperatures, represent actual physical facts, but the values of θ_2 and $\frac{1}{2}(\theta_1+\theta_2)$ can only be regarded as an approximation to the probable behaviour of the solutions at higher temperatures.

The values of θ_1 and θ_2 are deduced as follows. By differentiating the logarithmic equation we get

$$\frac{1}{K}\frac{dK}{dt} = \frac{n}{t+T} - \frac{a}{\mu} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (1),$$

where μ is the modulus 0·4343.

A second differentiation gives

$$\frac{1}{K}\frac{d^2K}{dt^2} - \frac{1}{K^2}\left(\frac{dK}{dt}\right)^2 = -\frac{n}{(t+T)^2} \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad (2).$$

Putting $d^2K/dt^2 = 0$, and substituting from (1) we get

$$\left(\frac{n}{t+T} - \frac{a}{\mu}\right)^2 = \frac{n}{(t+T)^2}, \text{ whence}$$

$$\frac{n \pm \sqrt{n}}{t+T} = \frac{a}{\mu};$$

and the points of inflexion are given by

$$\theta_1 = \frac{\mu}{a}(n - \sqrt{n}) - T, \text{ and } \theta_2 = \frac{\mu}{a}(n + \sqrt{n}) - T.$$

For the temperature of maximum molecular conductivity we put $dK/dt = 0$ in (1), and obtain for t the value $t = \mu n/a - T = \frac{1}{2}(\theta_1 + \theta_2)$; so that the temperature of maximum conductivity is the mean between the two "tropical temperatures" θ_1 and θ_2.
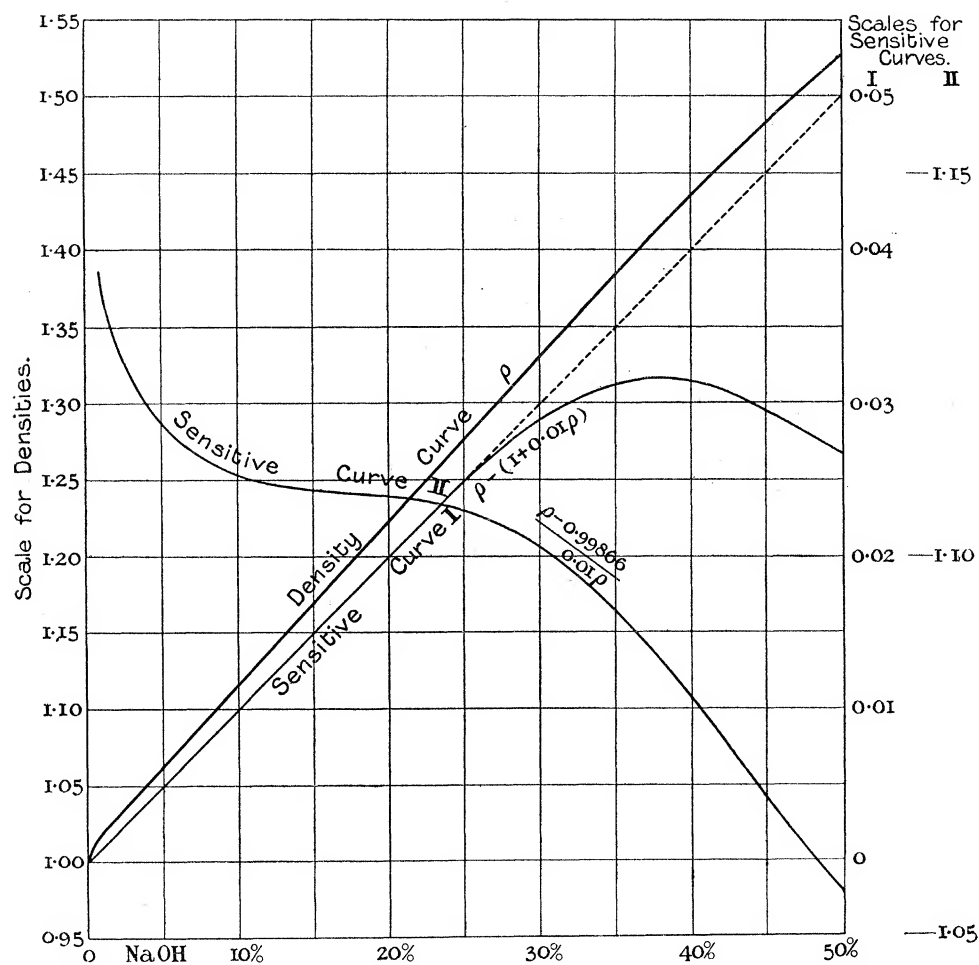
Diagram I.   Density of aqueous solutions of sodium hydroxide, with sensitive curves.

(See p. 270.)
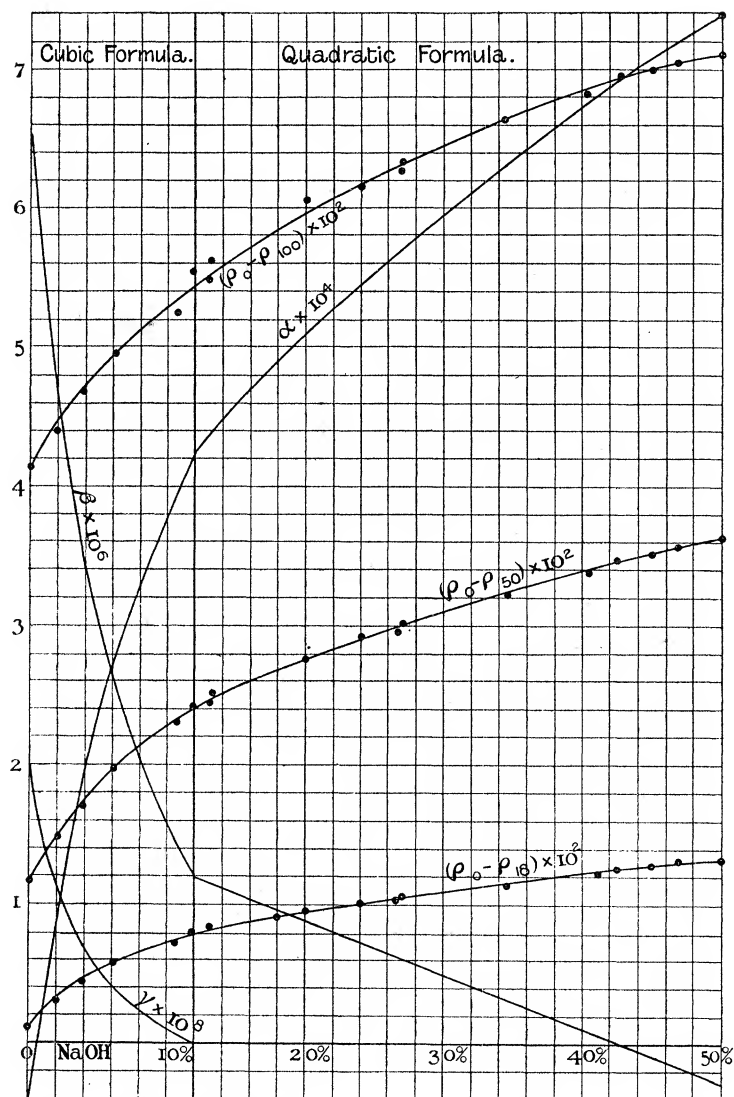
Diagram II.   Expansion of aqueous solutions of sodium hydroxide.   Difference curves for $\rho_0 - \rho_{18}$, $\rho_0 - \rho_{50}$, and $\rho_{50} - \rho_{100}$, and coefficients in the equation $\rho_t = \rho_0 + \alpha t + \beta t^2 + \gamma t^3$.

(See p. 277.)
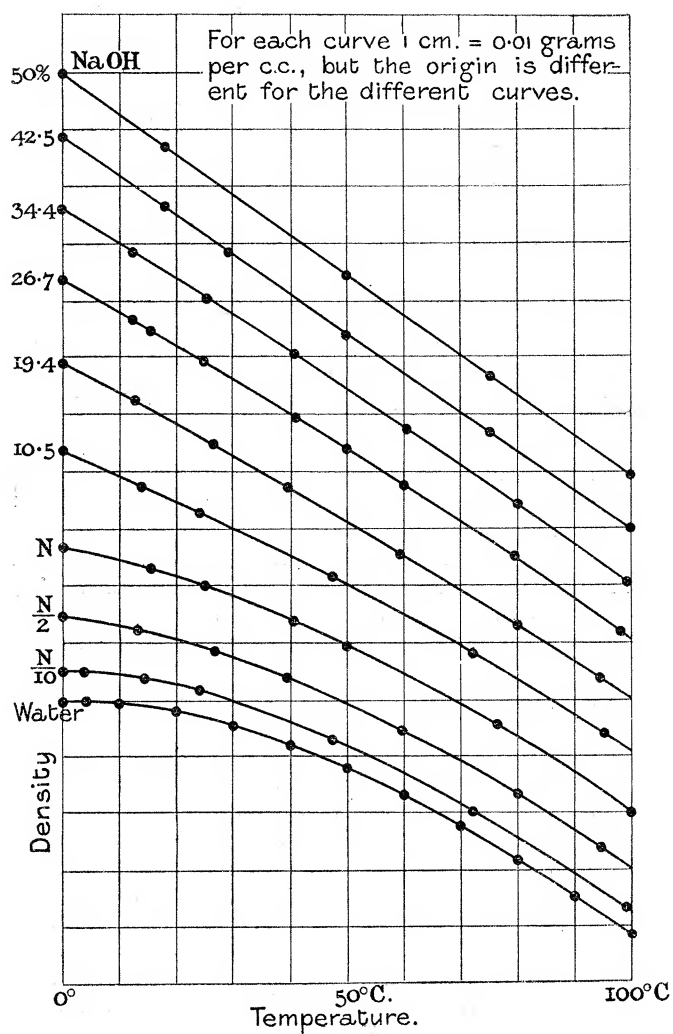
Diagram III.   Density-temperature curves for aqueous solutions of sodium hydroxide.

(See p. 280.)
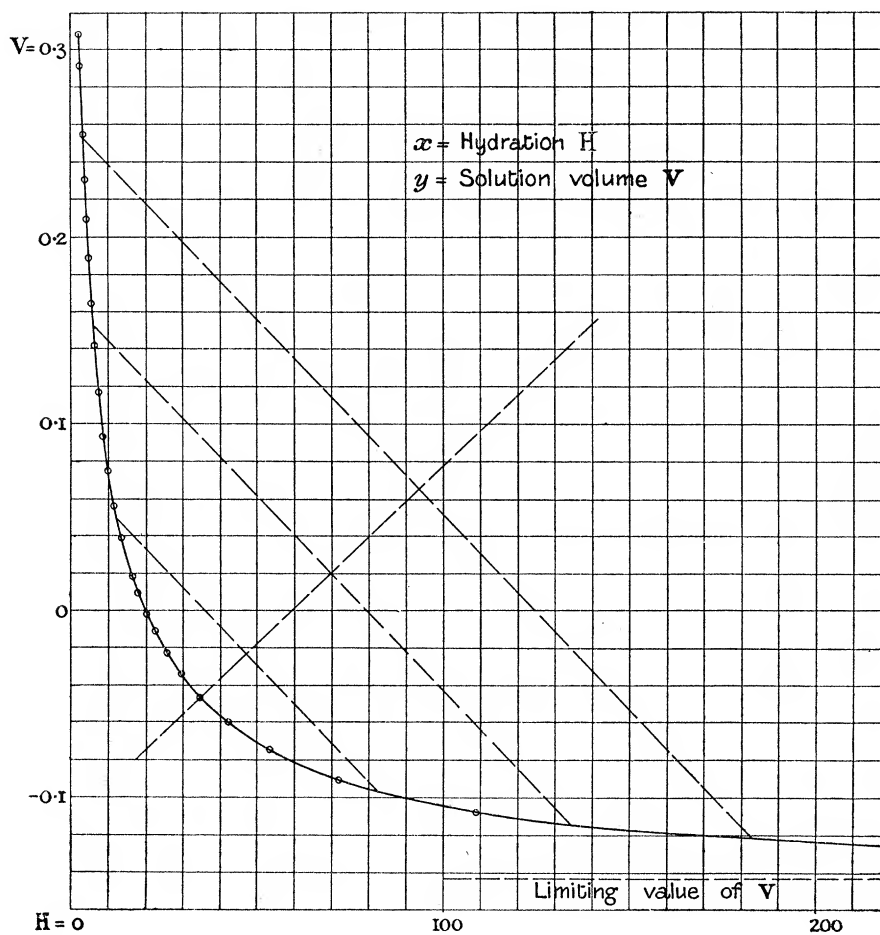
Diagram IV.   Solution volume of 1 gramme of soda at 18° C., plotted against the hydration of the
solution expressed in molecules of water per molecule of soda.

(See p. 281.)
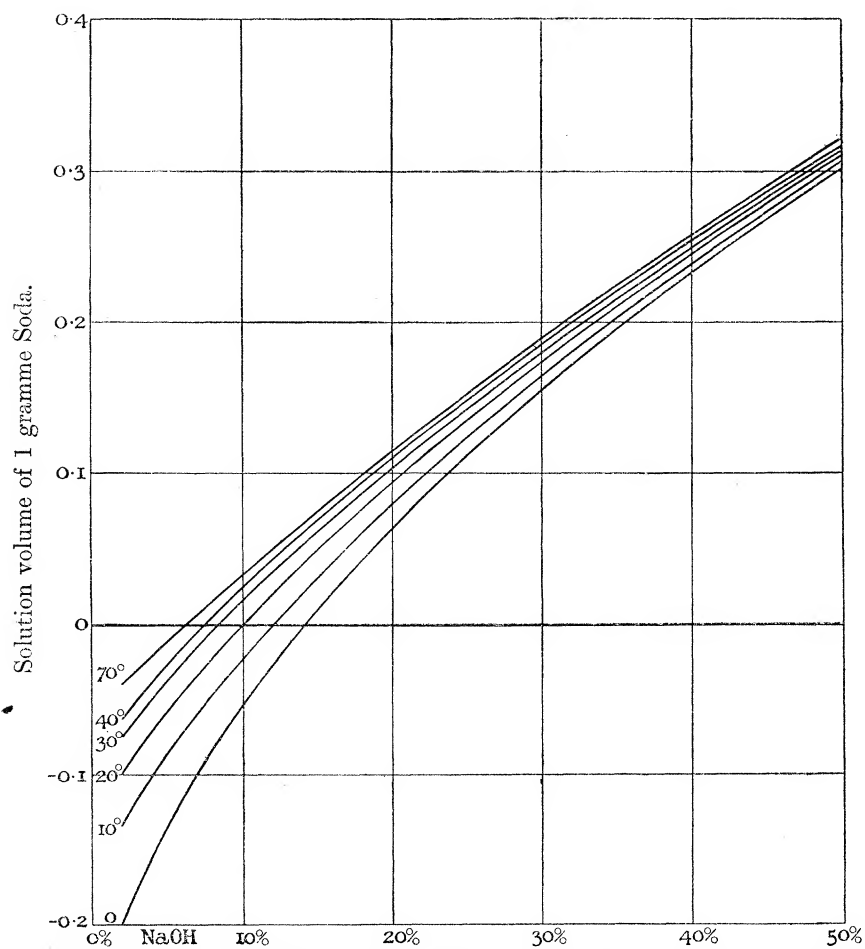
Diagram V.   Variation of solution volume with concentration at different temperatures.

(See p. 282.)
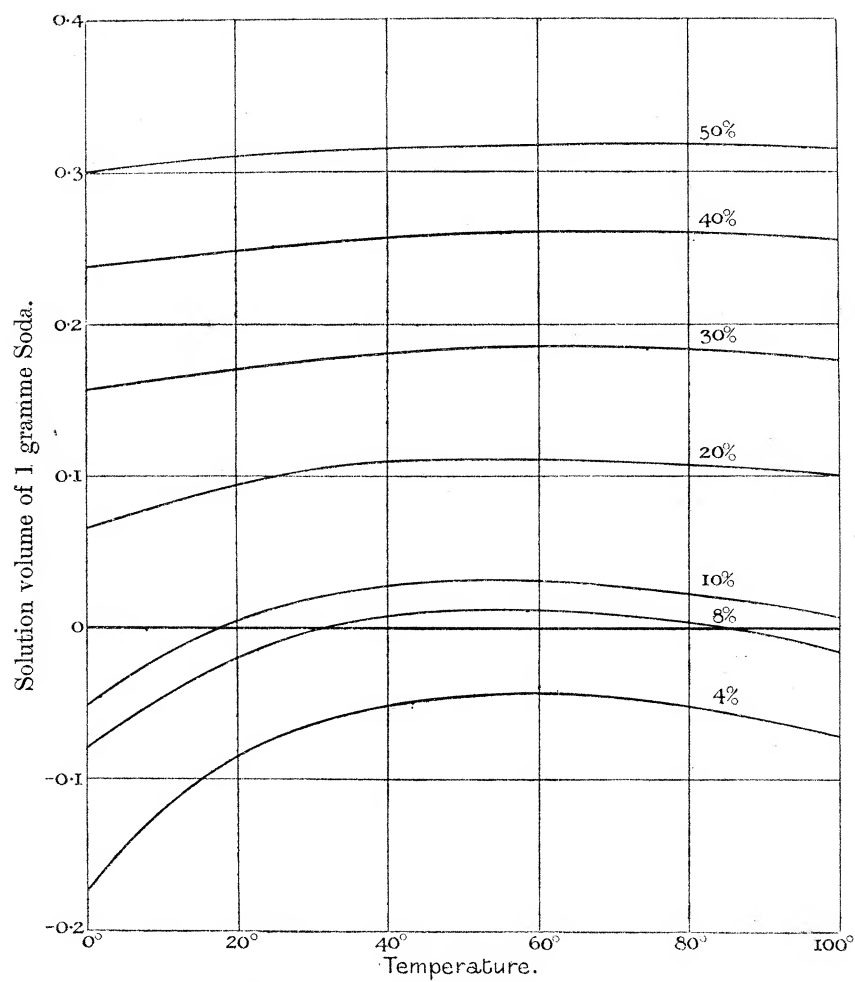
Diagram VI.   Variation of solution volume with temperature.

(See p. 282.)

Conductivity of Soda at 18° C.
x = Percentage of Soda
y = Conductivity $\varkappa_{18}$

○ = Observations of Kohlrausch
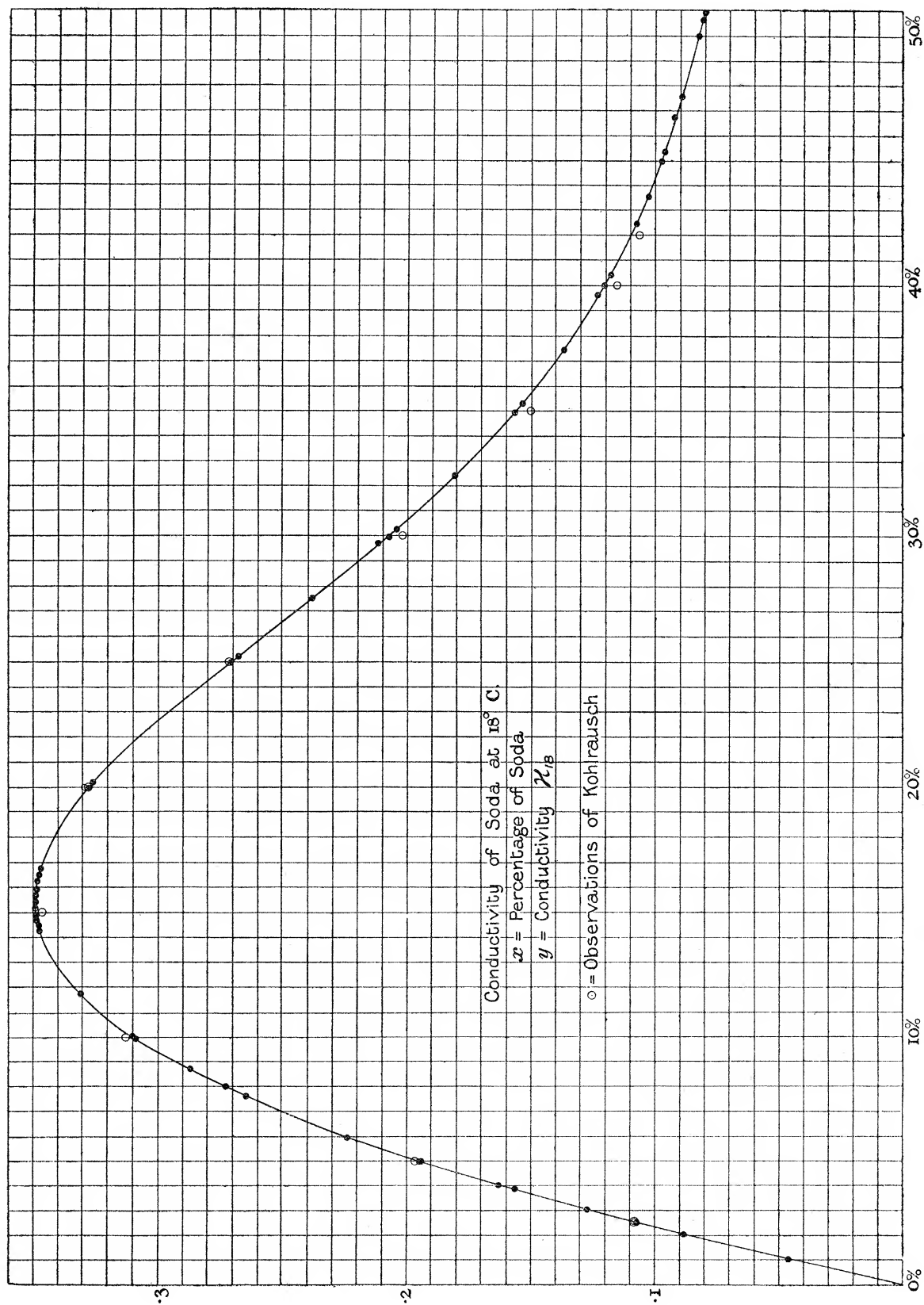
Diagram VII.   Isothermal conductivity-concentration curve for 18° C.   (See p. 287.)
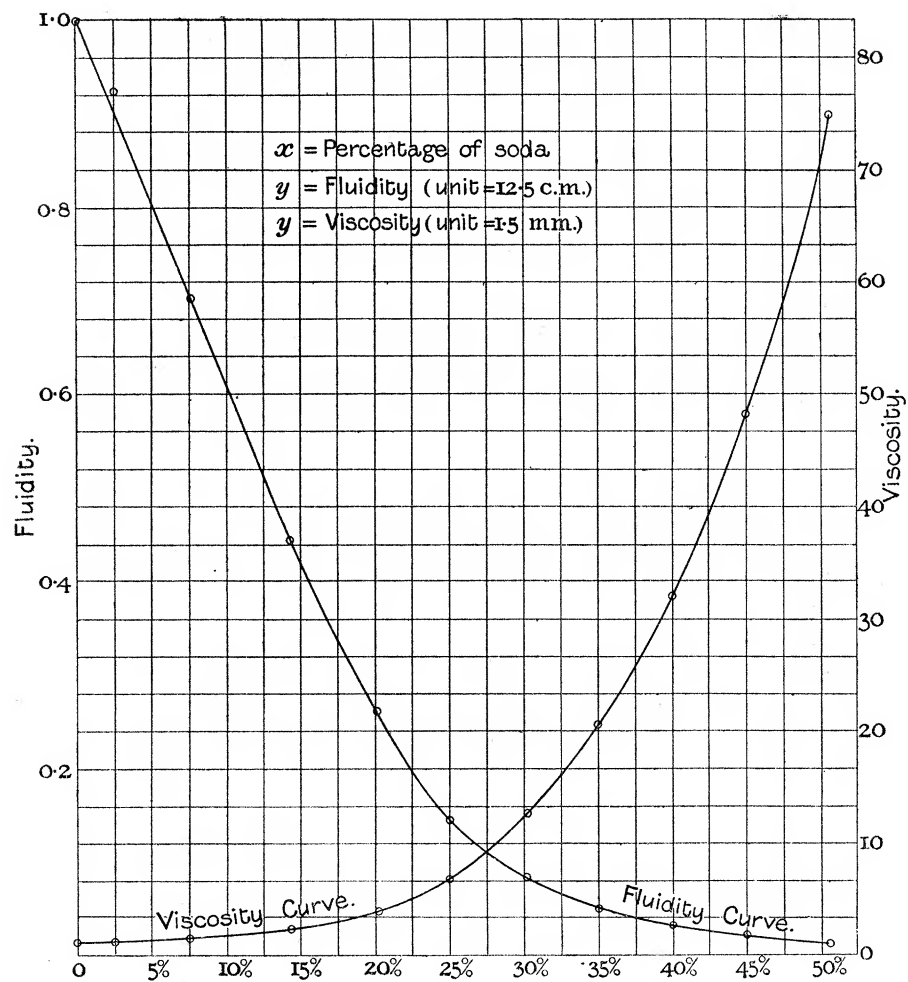
Diagram VIII.   Fluidity and viscosity of aqueous solutions of sodium hydroxide at 18° C.

(See p. 292.)
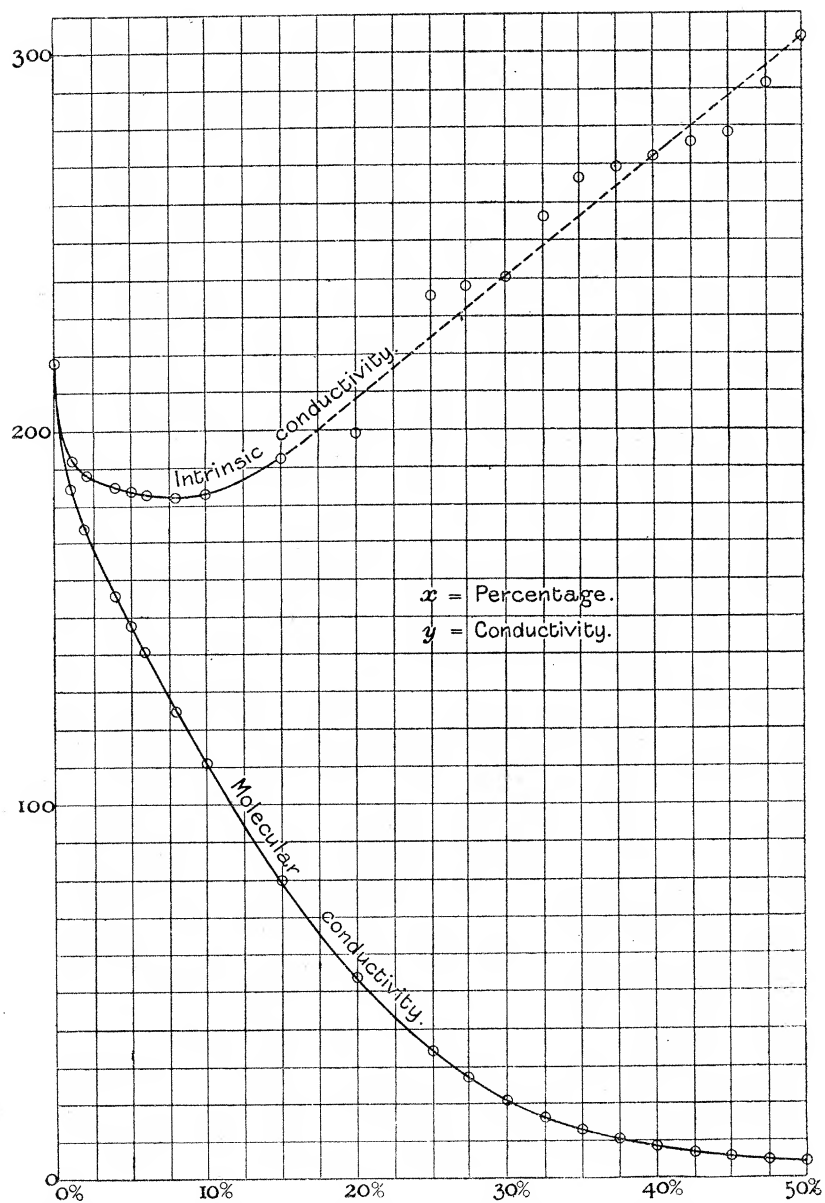
Diagram IX.   Molecular and intrinsic conductivity of sodium hydroxide in aqueous solutions
at 18° C.
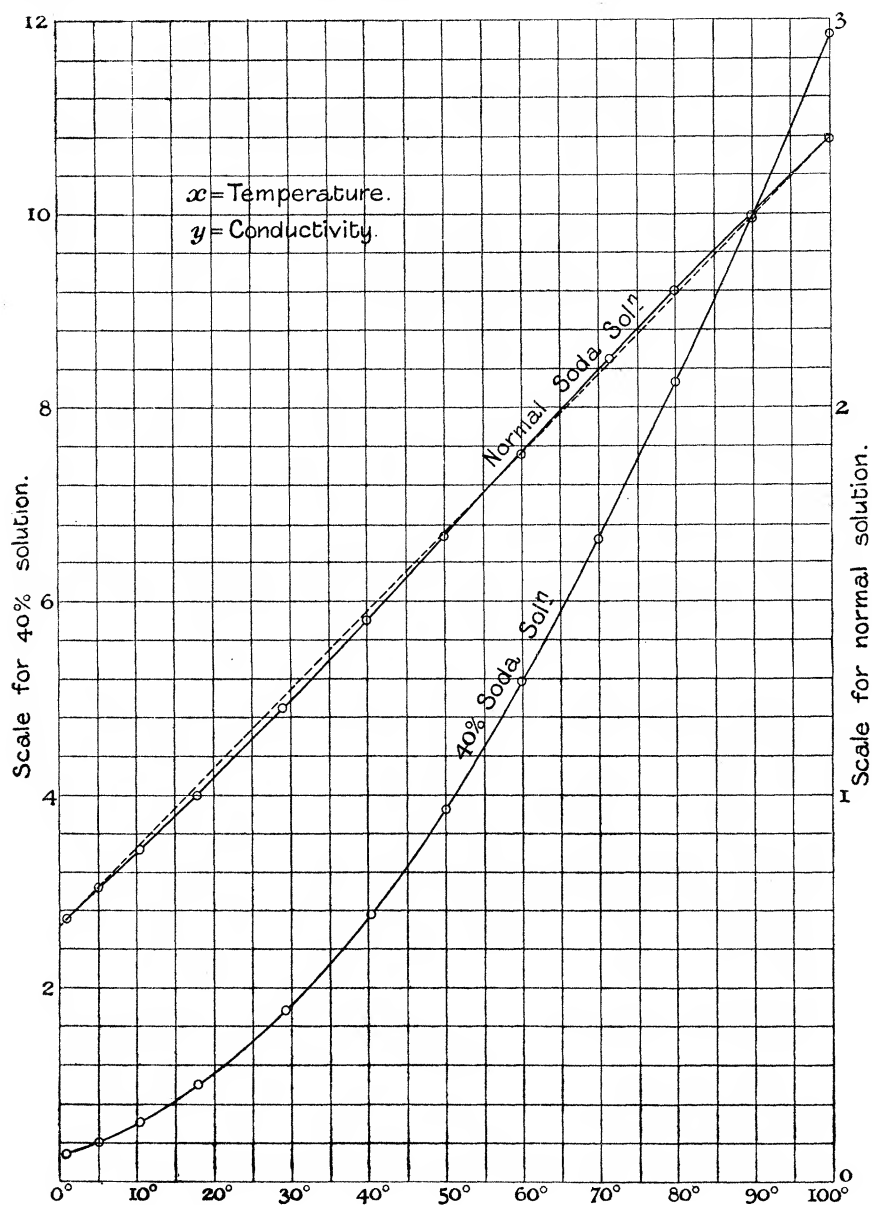
Diagram X.   Typical conductivity-temperature curves for concentrated and dilute solutions.   In each case the specific conductivity at 18° C. is taken as unity.   (See p. 301.)
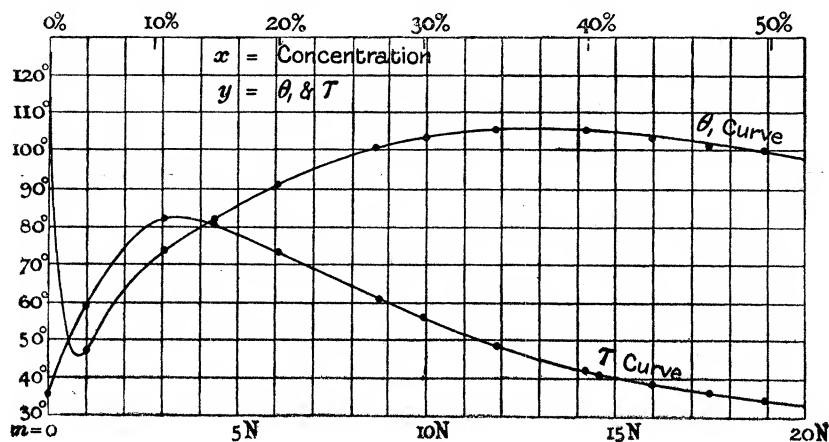
Diagram XI.   Variation of temperature of inflexion, θ_1, and conductivity zero, T, with concentration.
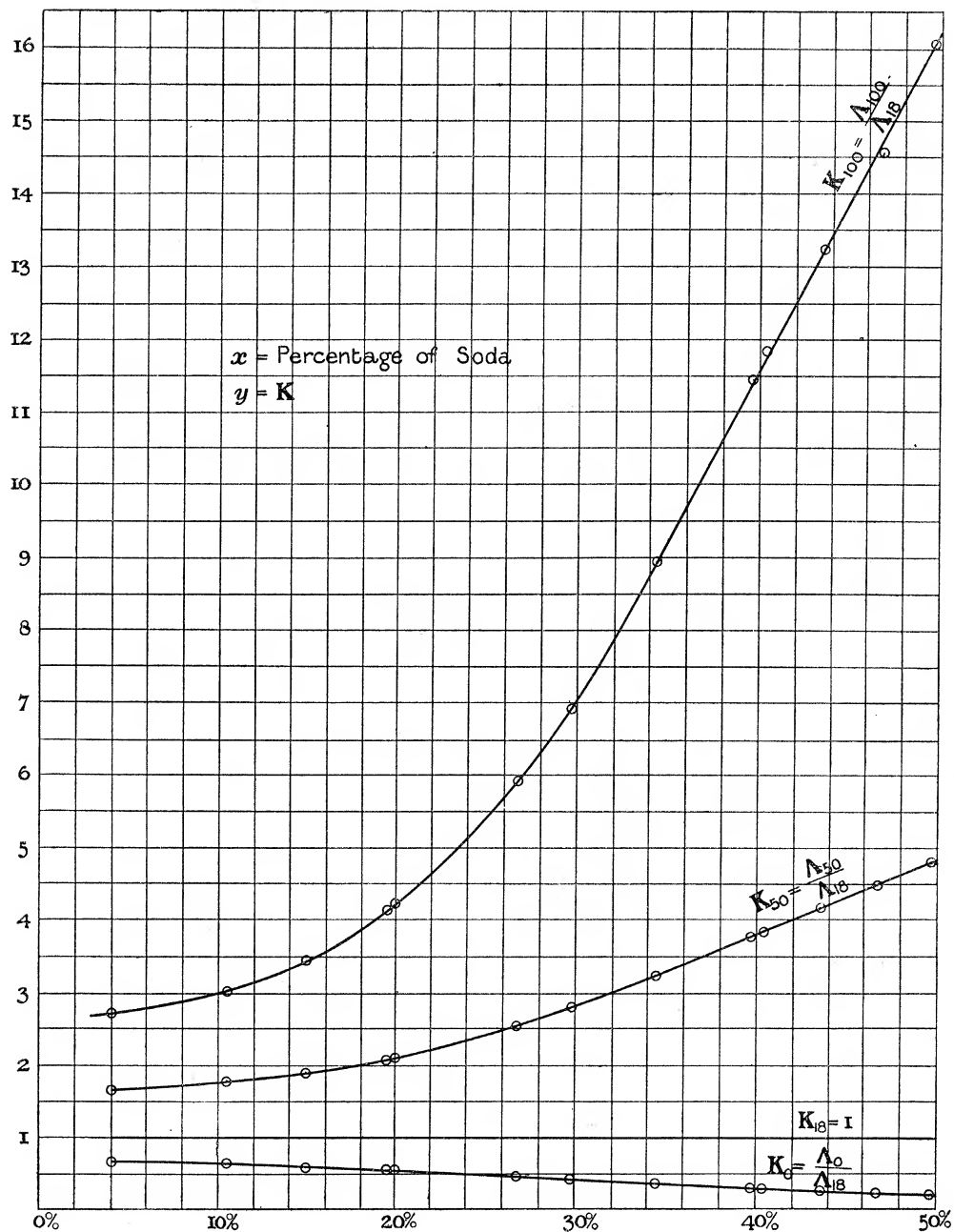(See p. 301.)

Diagram XII.   Influence of temperature on molecular conductivity.   In each case the molecular conductivity at 18° C., Λ_{18}, is taken as unity.
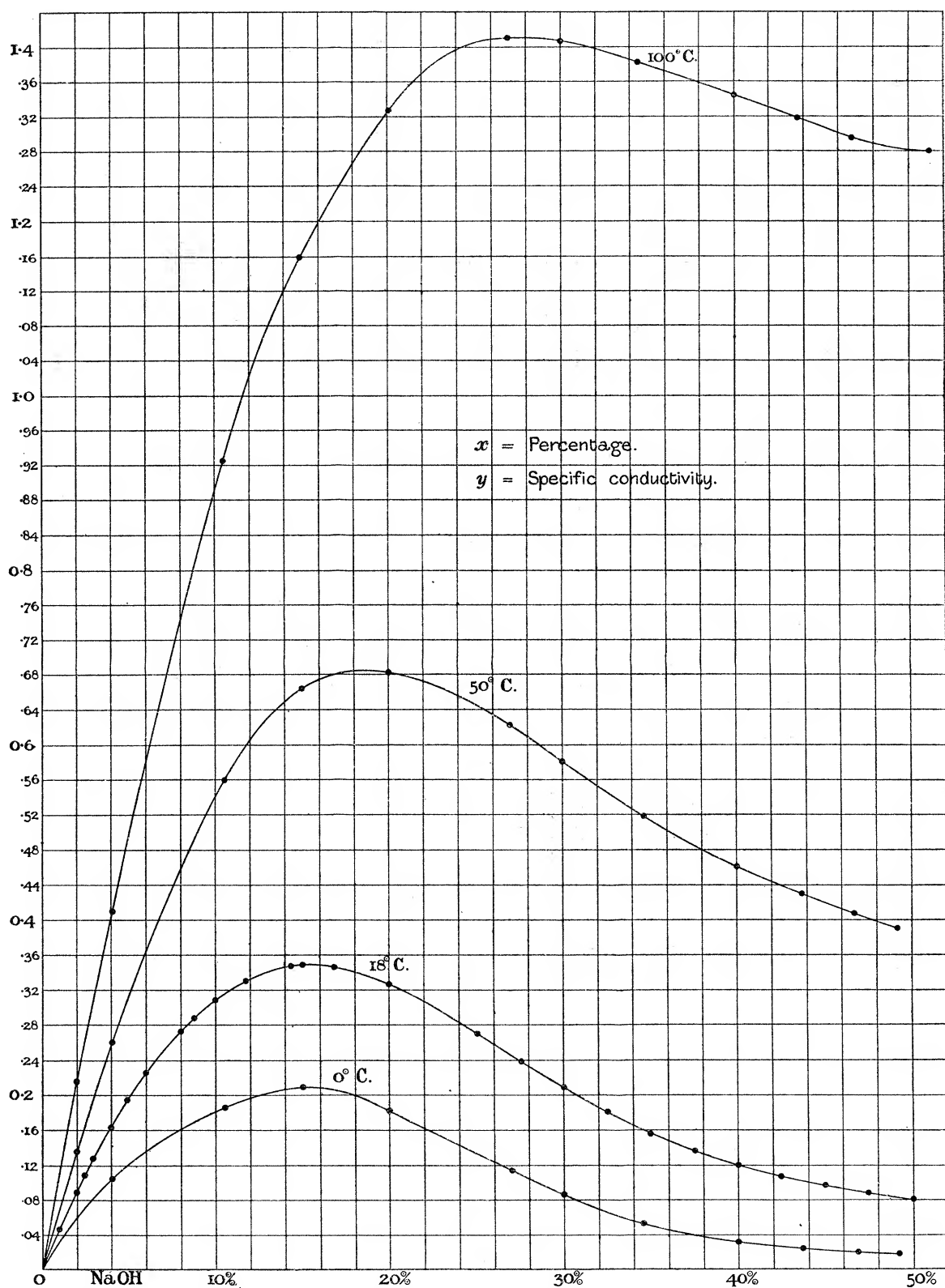
(See p. 305.)

Diagram XIII.   Isothermal conductivity-concentration curves for 0° C., 18° C., 50° C. and 100° C.
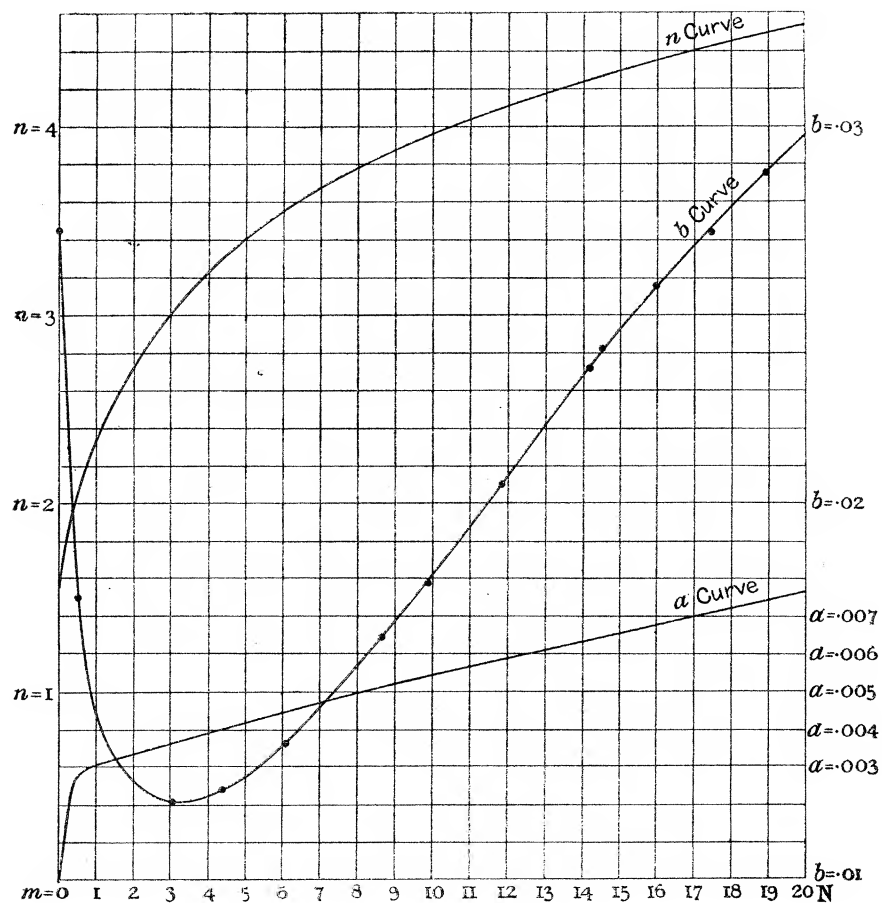
(See p. 302.)

Diagram XIV.   Coefficients in the equation $\dfrac{\kappa_t}{\kappa_0} = \dfrac{\rho_t}{\rho_0}(1 + bt)^n \, 10^{-at}$.

(See pp. 301 and 302.)